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DEVELOPMENT OF THE CATALYTIC CHAMBER PROCESS FOR THE MANUFACTURE OF SULFURIC AND NITRIC ACIDS FROM WASTE FLUE GASES

by

B. Keilin
A. L. Walitt

Final Report, Contract No. PH 86-68-75

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A process has been developed for the simultaneous removal of sulfur dioxide and nitrogen oxides from power plant flue gas at normal stack gas effluent temperatures. Sulfur dioxide removal is accomplished by oxidation with nitrogen dioxide followed by absorption of the resulting sulfuric acid and the oxides of nitrogen in a recycle stream of sulfuric acid. The acid is stripped of its nitrogen oxide content and is recirculated to the absorber after the product acid is withdrawn. The nitrogen oxides are reoxidized with the excess nitrogen dioxide being converted to nitric acid and the bulk of the oxide recycled for further sulfur dioxide oxidation. Thus the nitrogen dioxide acts as a reactive catalyst. A high temperature isothermal scrubber permits the scrubber to recover the sulfuric acid and the oxides of nitrogen without absorbing any diluent water (which would require heat to remove), and a catalytic stripper which rapidly oxidizes the oxides of nitrogen in the liquid phase, thus avoiding the vapor pressure limitations of recovering a dissolved gas from solution and thereby eliminating the need for extra heat. Experimental confirmation on a limited laboratory scale was obtained for these two vital parts. Activated charcoal was used as the catalyst to oxidize the NO_x. In addition, kinetic studies of the sulfur dioxide oxidation reaction with nitrogen dioxide were conducted which established the practicality of performing this reaction at the low concentration levels present in power plant flue gas. A 10 SCFM pilot plant was constructed for use in evaluating the various process stages. A preliminary economic analysis based on an 800 megawatt power plant, producing 1.44 million standard cubic feet per minute of flue gas, showed that an add-on clean-up plant would cost about 11.3 million dollars in capital costs and about 3.7 million dollars per year in operating costs before taking a credit for acid by-products. Even if HNO_3 recovery were not desirable, sale of sulfuric acid at a mere $14 per ton (100% basis) would recover the total operating cost.

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I. SUMMARY

A process has been developed for the simultaneous removal of sulfur dioxide and nitrogen oxides from power plant flue gas at normal stack gas effluent temperatures. The process, based on the Lead Chamber Process for sulfuric acid manufacture, incorporates two technological breakthroughs developed on this contract to produce sulfuric acid and nitric acid without the need for additional raw materials or heat beyond that in the flue gas. Sulfur dioxide removal is accomplished by oxidation with nitrogen dioxide followed by absorption of the resulting sulfuric acid and the oxides of nitrogen in a recycle stream of sulfuric acid. The acid is stripped of its nitrogen oxide content and is recirculated to the absorber after the product acid is withdrawn. The nitrogen oxides are reoxidized with the excess nitrogen dioxide being converted to nitric acid and the bulk of the oxide recycled for further sulfur dioxide oxidation. Thus the nitrogen dioxide acts as a reactive catalyst.

The two major modifications to the original Chamber Process which make this new method technologically and economically feasible are: a high temperature isothermal scrubber which permits the scrubber to recover the sulfuric acid and the oxides of nitrogen without absorbing any diluent water (which would require heat to remove), and a catalytic stripper by which the oxides of nitrogen in the scrubber effluent acid are rapidly oxidized in the liquid phase, thus avoiding the vapor pressure limitations of recovering a dissolved gas from solution and thereby eliminating the need for extra heat.

Experimental confirmation on a limited laboratory scale was obtained for the two vital parts of the new Catalytic Chamber Process: high temperature absorption of sulfuric acid and nitrogen oxides in sulfuric acid, and catalytic oxidation of nitrogen oxide solutions in sulfuric acid

[illegible] to oxidize the NO_x

solution to NO_2 using activated charcoal as the catalyst. In addition, kinetic studies of the sulfur dioxide oxidation reaction with nitrogen dioxide were conducted which established the practicality of performing this reaction at the low concentration levels present in power plant flue gas. A 10 SCFM pilot plant was constructed for use in evaluating the various process stages.

A preliminary economic analysis based on an 800 megawatt power plant, producing 1.44 million standard cubic feet per minute of flue gas, showed that an add-on ~~Catalytic Chamber~~ Process clean-up plant would cost about 11.3 million dollars in capital costs and about 3.7 million dollars per year in operating costs before taking a credit for acid by-products. If 80% sulfuric acid and 52% nitric acid can be sold for $20 and $40 per ton (100% basis) respectively, the plant can make a gross pretax profit of 2.5 million dollars per year.

If the sulfuric acid could be sold for only $12.50 per ton (100% basis) and nitric acid sold for $40 per ton, the plant would still make a gross, pretax profit of about $0.58 million per year. Even if HNO_3 recovery were not desirable and therefore not provided for at a given location, sale of sulfuric acid at a mere $14 per ton (100% basis) would recover the total operating cost.

In addition to its application to the removal of pollutants from power plant stack gases, the Catalytic Chamber Process may provide a possible alternative to currently used methods of manufacturing sulfuric acid from conventional sources of sulfur dioxide. Since the nitrogen oxides are oxidized separately from the sulfur dioxide oxidation reaction, and consequently there is no longer a difficulty in removing the nitrogen oxides from concentrated sulfuric acid solution, it would now be possible to operate the Lead Chamber Process at high acid strengths, thus removing the major drawback to this currently obsolete process. The Catalytic Chamber Process appears to be the first significant, new process concept for sulfuric acid manufacture to be suggested in the past 50 years.

II. RECOMMENDATIONS

The Catalytic Chamber Process which is presented in detail in Section III has been conceptualized on the basis of somewhat incomplete supporting experimental work. The process stages of major interest: high temperature sulfuric acid and nitrogen oxide absorption, and catalytic oxidation of nitrogen oxides have been individually confirmed on a laboratory scale, but no work has been performed on an integrated, continuous basis. In addition there are areas which are virtually impossible to evaluate on a small scale (such as the need for mist eliminators) thus making it imperative that the scale of work be expanded. The following recommendations for future work are made with those considerations in mind:

A. Catalyst Evaluation

The activated charcoal catalyst used in the small scale experimentation appears to have stability problems which must be evaluated. In addition, it is important that the field of catalysts be properly screened to see which is the best catalyst to use. There are many candidate materials and only one has been tested.

B. Pilot Plant Conversion and Operation

The pilot plant is currently set up to evaluate an early version of the Catalytic Chamber Process and it is necessary to convert to equipment to conform with the latest system including the high temperature scrubber and the catalytic stripper. This should be the first item of business in a continued research program.

C. Demonstration Plant Design

As soon as the general feasibility of the Catalytic Chamber Process is established work should commence on a scale-up beyond the 10 SCFM capability of the current pilot plant. It is strongly recommended that design work begin as soon as possible on a 1000 SCFM demonstration plant which would put all the process problems on a realistic basis. Such things as the need for mist eliminators, the ability to control the composition of gases in the process and the realistic limit on absorption efficienty can only be fully evaluated at the 1000 SCFM scale. In conjunction with this an economic evaluation of the capital and operating costs should be undertaken.

III. INTRODUCTION

During the past several years the problem of air pollution from power plant stack gases has received much attention from government and civic agencies with the result that a great deal of research and development effort has been devoted to the clean-up of these contaminated gases. The primary offender in stack gases is sulfur dioxide (3000-6000 ppm), although the nitrogen oxides present are also considered detrimental to human, plant and animal life.[1]

Historically, contaminated gaseous effluents from plant stacks have been treated in wet scrubbers to remove undesirable components, but these wet processes have the disadvantages of releasing a gas of low temperature and high water content which prevents its ready dissipation in the atmosphere. More recently several dry processes have been proposed which avoid these problems.

Oxidation of the SO_2 to SO_3 and recovery of the sulfur values as sulfuric acid results in a low operating cost because no raw materials are needed. A route to effect the oxidation of SO_2 to sulfuric acid and remove NO_x as well as SO_2 from power plant stack gases is through the use of nitrogen dioxide as a reactive, regenerable catalyst in a manner similar to the old Lead Chamber Process technique. The work on this contract (NAPCA PH86-68-75) was undertaken to determine the ability of NO_2 to oxidize the dilute SO_2 present in flue gas in a recycling scheme in which the NO produced from the SO_2 oxidation reaction is reoxidized to NO_2 and thus is available for reuse. This report describes the conceptual progress made during the 21 months of the contract as well as the experimental work performed to support the theory.

IV. CURRENT PROCESS

A. General

This section of the report will discuss the process concept in its most advanced form. The fundamental aspects of the process have been established experimentally although it has not been operated in an integrated manner. The process will be described, experimental verification given and future plans presented. A process flow sheet, heat and material balances and a preliminary economic evaluation will be presented. Succeeding sections will discuss the original process concept and will follow its evolution to the current system including the experimental support work done throughout the contract period. The discussion will include the breakthroughs that make this process feasible and the potential impact of these developments on the sulfuric acid industry in general.

B. The Catalytic Chamber Process

The most recent conceptualization of the Tyco/NAPCA process for the removal of SO_2 and NO_x from power plant stack gas has been named the Catalytic Chamber Process because of the novel manner in which the oxides of nitrogen are recovered and oxidized for reuse as the SO_2 oxidant. In this process, (see Flow Sheet, Figure 1) the raw flue gas, having had most of the fly ash removed, is contacted with a stream of recycle NO_2 which oxidizes the SO_2 to SO_3, which hydrolyzes to sulfuric acid through contact with water vapor in the gas stream. The reacted gases pass through a sulfuric acid scrubber which removes the newly formed acid and the oxides of nitrogen and the cleaned, wet stack gas is vented to the atmosphere at relatively high temperature, insuring easy dissipation. The nitrogen oxide-bearing sulfuric acid (nitrose) is passed on to a stripper column where it is contacted with a catalyst (activated charcoal, for example) counter-current to a small side stream of the raw flue gas. Here the oxides of nitrogen are catalytically oxidized to NO_2 in the liquid phase with the flue gas providing the necessary oxygen. The gas stream from the stripper, now containing all the oxides of nitrogen as NO_2 and some of the flue gas is passed through a water scrubber which recovers the excess NO_2 (equivalent to the net NO_x recovered) as nitric acid before being mixed with the bulk of the flue gas stream for further SO_2 oxidation.

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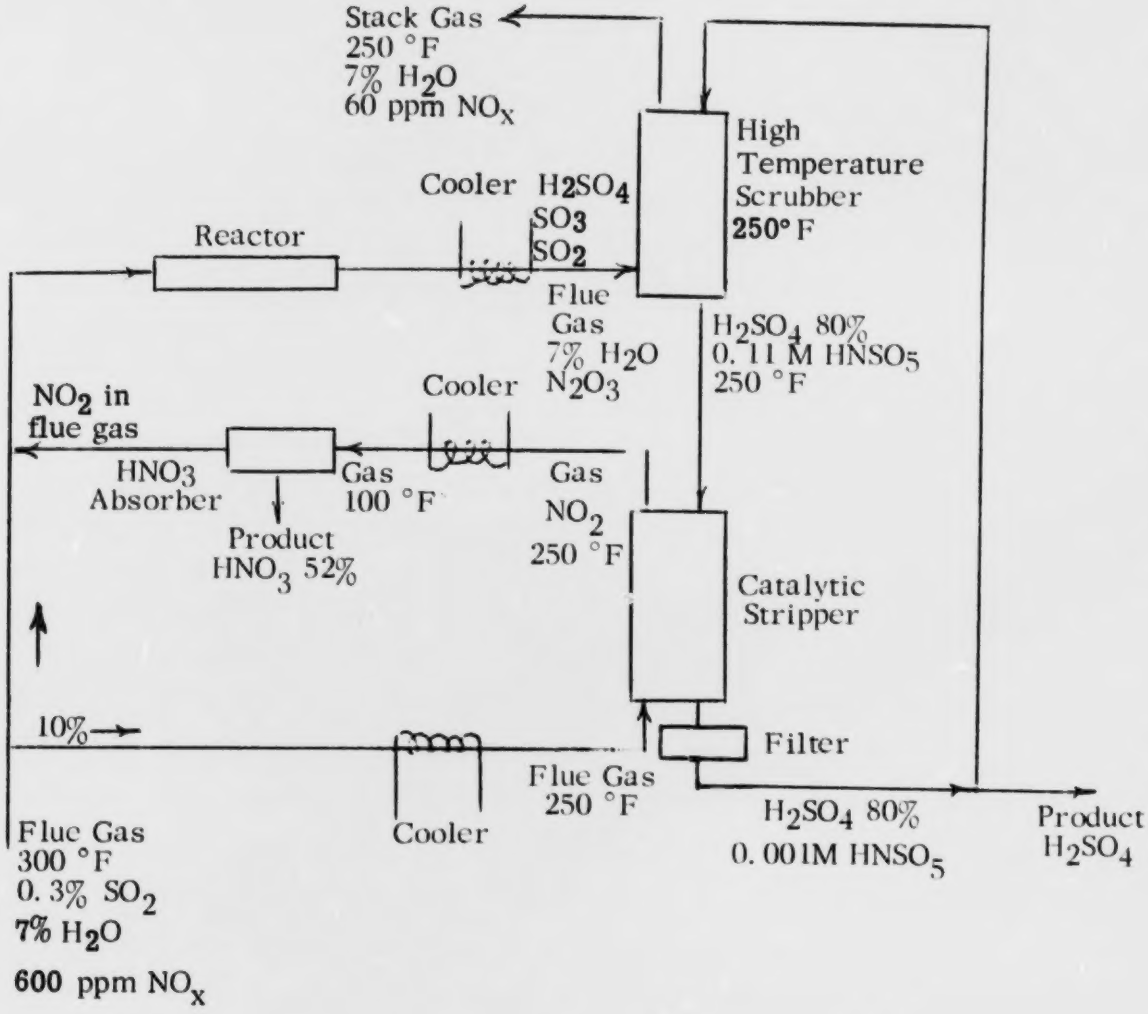

Stack Gas
250 °F
7% H_2O
60 ppm NO_x
High
Temperature
Scrubber
250° F
Cooler
H_2SO_4
SO_3
SO_2
Reactor
Flue
Gas
7% H_2O
N_2O_3
H_2SO_4 80%
0. 11 M $HNSO_5$
250 °F
NO_2 in
flue gas
Cooler
HNO_3
Absorber
Gas
100 °F
Gas
NO_2
250 °F
Product
HNO_3 52%
Catalytic
Stripper
10%
Filter
Flue Gas
250 °F
H_2SO_4 80%
0. 001M $HNSO_5$
Product
H_2SO_4
Flue Gas
300 °F
0. 3% SO_2
7% H_2O
600 ppm NO_x
Cooler

Fig. 1. Catalytic Chamber Process

An amount of sulfuric acid equivalent to the SO_2 recovered is removed as product from the denitrated acid leaving the stripper before the acid is returned to the scrubber for recycle.

Table I shows a complete material balance for the process shown in Figure 1 along with the temperatures of the various process streams. Table II presents an energy balance for the system on the same basis as the material balance. Examination of these tables will show that the process requires no additional heat (in fact, it is exothermic overall) and a minimum of cooling water; both facts contribute markedly to the low operating cost which will be itemized later.

C. Flue Gas Condition

It is obvious that the composition and temperature of the power plant flue gas will vary with the plant being treated, depending on such things as ambient temperature and humidity, type of fuel, size of the plant, efficiency of heat recovery and anti-pollution control devices already in use. Rather than try to cover a whole range of conditions, the following "average" gas composition was assumed, based on OAP's recommendation, and was used throughout the study:

CO_2	14.6% V
H_2O	7.3% V
SO_2	0.3% V (6400 ppm by weight)
O_2	2.8% V
N_2	74.8% V
NO_x	0.06% V (600 ppm by weight)
Ash	0.2% wt
Temperature	300° F

The effect of the fly ash on the operation of the process is of some interest although by the very nature of the process, its influence is minimized. Most power plants have some type of dust collection system to clean up the stack gas before it is vented to the atmosphere, thus partially solving the problem. If an appreciable amount of ash is introduced to the proposed SO_2 clean-up system, there are three ways to approach the problem:

Table I. Material Balance for Catalytic Chamber Process*

Stage	CO_2	H_2O	SO_2	O_2	N_2	H_2SO_4	Ash	NO_2	NO	Total	Temp., °F
Gas from stack	215	44	6.4	30	702	—	2.0	0.06	0.54	1000	300
Gas to stripper	21.5	4.4	0.64	3.0	70.2	—	0.2	0.006	0.054	100	250
Gas from stripper	21.5	3.97	—	1.18	70.2	—	—	10.48	—	107.33	250
Gas to HNO_3 absorber	21.5	3.97	—	1.18	70.2	—	—	10.48	—	107.33	100
Gas from HNO_3 absorber	21.5	3.97	—	1.18	70.2	—	—	9.42	0.23	106.50	100
Water to HNO_3 absorber	—	1.03	—	—	—	—	—	—	—	1.03	70
Product HNO_3 (52%)	—	0.89	—	—	—	—	—	0.97 (HNO_3)	—	1.86	100
Gas to reactor	215	43.57	5.76	28.18	702	—	1.8	9.43	0.75	1006.49	300
Gas to scrubber	215	41.95	—	28.18	702	8.82	1.8	5.28	3.45	1006.48	250
Gas to stack	215	39.75	—	28.18	702	—	—	0.091	0.059	985.08	250
Acid to scrubber	—	716	—	—	—	2864	—	0.053	0.034	3580.087	250
Acid from scrubber	—	718.21	—	—	—	2872.82	1.8	5.24	3.43	3601.50	250
Acid from stripper	—	718.5	—	—	—	2873.8	2.0	0.053	0.034	3594.387	250
Acid from filter	—	718.23	—	—	—	2872.74	—	0.053	0.034	3591.057	250
Cake from filter	—	0.27	—	—	—	1.06	2.0	~	~	3.33	250
Product H_2SO_4 (80%)	—	2.23	—	—	—	8.74	—	~	~	10.97	250

* Assumptions:

1. Basis: 1000 lb of entering flue gas
2. 10% of flue gas passed through the stripper
3. Stripper is 99% efficient in denitrating the scrubber acid
4. Scrubber is 99% efficient in NO_x recovery
5. All SO_2 entering stripper oxidized by NO_2 and scrubbed out
6. Acid is filtered after the stripper and filter cake is 60% solids.

Table II. Energy Balance (Basis: 1000 lb FlueGas at 32°F)

Heat Inputs	Btu
Entering flue gas (1000 lb) (0. 25 Btu lb/lb/°F) (300 - 32)	67,000
Water into HNO_3 absorber (1. 3 lb) (1 Btu/ lb/ °F) (70 - 32)	39
Heat of reaction ($NC_2 + SO_2$) (9. 8 lb) (1350 Btu/ lb)	13,200
Heat of absorption (N_2O_3 + H_2SO_4) (8. 73 lb) (271 cal/g)(1. 8)	4,260
Heat of reaction ($H_2C + NO_2$) (0. 97 lb) (17. 2 cal/g) (1. 8)	30
Water absorbed in scrubber ($H_2O + SO_3 \rightarrow 80\%\ H_2SO_4$) (0. 09 mol/0. 8), (18 lb/mol) (967 Btu/lb)	1,950
Water absorbed in stripper ($HNSO_5 + H_2O$) (0. 2295 mol) (1/2) (18 lb/mol) (967 Btu/lb)	2,000
Total	88,479
Heat Outputs	
Stack gas effluent (985 lb) (0. 25 Btu/lb/°F) (250 - 32)	53,600
Product H_2SO_4 (12. 3 lb) (95 Btu/lb)	1,170
Heat of reaction ($HNSO_5 + O_2$) (0. 2298 mol) (8280 cal/mol) (1, 8)	3,430
Product HNO_3 (1. 86 lb) (0. 66 Btu/lb/°F) (100 - 32)	83

Table II - Continued

Heat Outputs	Btu
Cooling reacted flue gas (342 → 250 °F) (1007 lb) (0.25 Btu/lb) (342 - 250)	23,200
Cooling stripper gas for HNO_3 absorber to 100 °F (108 lb) (0.075) (0.25 Btu/lb/°F) (250 - 100)	300
Cooling scrubber (heat of absorption — $N_2O_3 + H_2SO_4$) (8.73 lb) (271 cal/g) (1.8)	4,260
Vaporization of water in scrubber (from $HNSO_5$ generation) (0.2295 mol) (1/2) (18 lb/mol) (967 Btu/lb)	2,000
Total	87,943

Error = 536/ 88,479 = 0.6%

1) Depending on the use of the acid and the amount of fly ash in the raw flue gas, the ash can be ignored and the acid sold with a small amount of suspended solids. This might well be possible for acid sold to the fertilizer industry where acid purity is not critical.

2) Precipitation equipment could be added to the flue gas stream prior to entering the SO_2 removal plant to remove the bulk of the ash.

3) The ash could be allowed to enter the system with the gas which would be scrubbed clean of ash in the scrubber section. The acid could then be filtered either downstream of the scrubber or downstream of the stripper, although the soluble ash compounds would still be present in the acid.

One of the controlling factors in this problem is the effect of the ash on the catalyst in the stripper. If the ash acts as a poison for the catalyst, then it would have to be removed before it entered the stripper column. Since the catalyst has not been chosen and the effect of the ash is not known, this area has not received a great deal of emphasis. The solution is straightforward: filtration of the acid, with the effect of the ash on the overall process not being of concern to us at this time. (The one point of some interest; the solubility of the ash in sulfuric acid has been examined and the experimental results showing very low ash solubility can be found in Section V-G.) Since the soluble ash compounds could not be filtered out, the catalyst would have to be resistant to the compounds.

D. Oxidation Reaction Vessel

The purpose of the reactor is to provide sufficient volume to allow the oxidation of the SO_2 to take the place according to the following reaction:

$$SO_2 + NO_2 \rightarrow SO_3 + NO$$

The SO_3 is quickly hydrolyzed by the large excess of water vapor present in the flue gas forming sulfuric acid mist which remains in the gas stream. There is the possibility that some of this acid will condense on the walls of the reactor which should be considered when choosing materials of construction, but the greatest part of the acid will continue through the reactor to the scrubber. Sulfuric acid mist is a difficult material to remove from gases in general and there is no reason why an appreciable amount should condense in the reactor. The actual size of the reactor is controlled by the residence time required to effect complete oxidation of the SO_2 to SO_3. Under the gas conditions shown above, this reaction time is under 5 seconds as is shown by experimental verification in Section V-D. The total heat of reaction (see energy balance in Table II) is quite small in this dilute gas stream and the gas temperature is only raised from 300 °F to about 340 °F. This low temperature avoids the requirement for the large heat dissipating chambers needed in the standard Chamber Process and it is quite likely that in actual practice the reactor chamber will vanish altogether with the SO_2 oxidation occurring in the connecting ductwork. (The other reason for large chambers in the standard process, that of residence volume for the reoxidation of the nitric oxide formed in the SO_2 oxidation, is also avoided in the Catalytic Chamber Process by performing this oxidation catalytically in a separate stage. This will be discussed in detail later.)

E. High Temperature Scrubber

The reacted flue gases enter the scrubber as shown in Figure 2 and consist of inert gases, sulfuric acid mist, unreacted SO_2 and SO_3, water vapor and equimolar quantities of NO and NO_2. The reason the oxides of nitrogen must be in equimolar ratio is because individually NO and NO_2 are virtually insoluble in sulfuric acid while together they combine with sulfuric acid to form a crystalline material known as nitrosylsulfuric acid which is soluble in sulfuric acid up to 60% by weight:

$$NO_2 + NO + 2H_2SO_4 \rightarrow 2HNSO_5 + H_2O$$

Thus, in the scrubber the reacted gases are contacted with sulfuric acid which scrubs out the sulfuric acid mist, the nitrogen oxides and, depending on the acid temperature, the water vapor.

Here we are faced with one of the major problems attempting to apply Chamber Process technology to flue gas clean-up: the large excess of water in the stack gas above that which is needed to make sulfuric acid. In the standard Chamber Process the water to SO_2 mole ratio in the entering gas is 1:15 and more water must be added to make the acid. In the Tyco Catalytic Chamber Process this ratio in the flue gas is 25:1 and scrubbing this stream with cold sulfuric acid will cause dilution of the acid and create the necessity of reconcentrating the acid for recycle, an expensive, heat consuming process. The way around this is to scrub the reacted gases with hot sulfuric acid as is explained below.

If the gas is scrubbed with sulfuric acid at 80 °F as in the standard Chamber Process, all the water will be absorbed, thus diluting the acid. How-

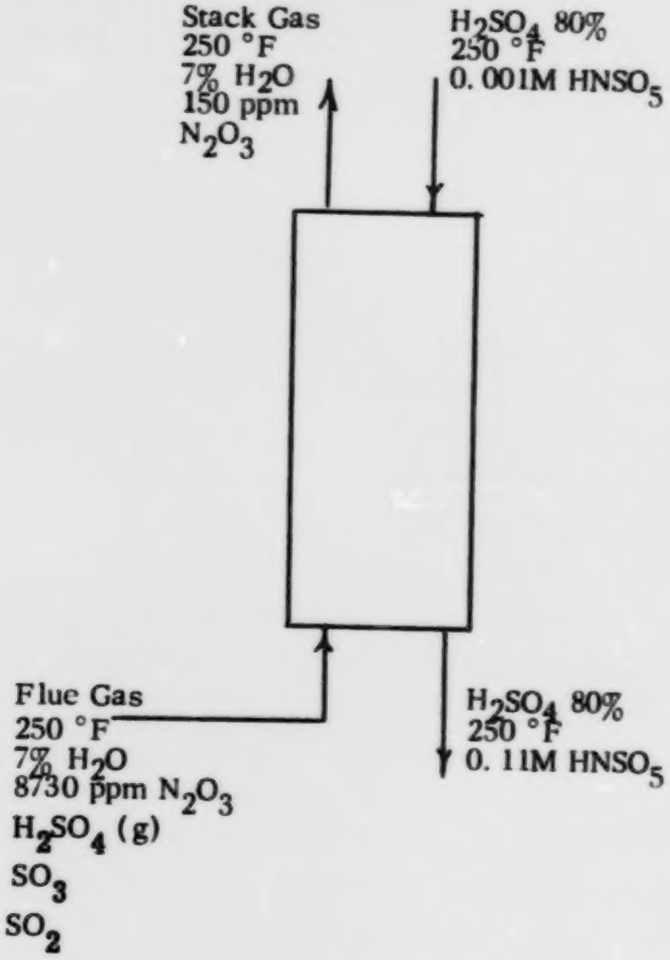

Stack Gas
250 °F
7% H_2O
150 ppm
N_2O_3
H_2SO_4 80%
250 °F
0.001M $HNSO_5$
Flue Gas
250 °F
7% H_2O
8730 ppm N_2O_3
H_2SO_4 (g)
SO_3
SO_2
H_2SO_4 80%
250 °F
0.11M $HNSO_5$

Fig. 2. High temperature scrubber

ever, if the column is run at a temperature where the vapor pressure of water over the incoming acid is equal to the partial pressure of water in the incoming gas, no water will be absorbed in the column and the acid will leave the scrubber at the same concentration as it entered. For 80% acid and a gas stream containing 7.3% water (52 mm Hg partial pressure), this temperature is 250°F (see Figure 3).

The question arises as to whether or not the oxides of nitrogen can be absorbed at this temperature. Using a small laboratory column in continuous counter-current flow it was found that about 99% of the oxides of nitrogen were removed by scrubbing with sulfuric acid at 250°F. The details of this work are given in Section V-K3 . It is clear that a scrubber operating at the appropriate temperature can remove the oxides of nitrogen as well as the sulfuric acid while permitting all the incoming water to pass into the atmosphere.

Of major importance is the ability of the scrubber to remove all sulfuric acid mist from the reacted flue gas. It has been determined experimentally (see Section V-J13) that on a pilot plant scale (10 SCFM) no measurable amounts of acid mist are able to pass through the scrubber when operated at the 100° F level. It is likely that no real engineering data can be determined on the acid mist problem until a pilot plant of 1000 to 100,000 SCFM capacity is in operation. More details on the scrubber effluent gas can be found in the section discussing the performance of the laboratory pilot plant (V-J13).

Since the solubility of nitrosylsulfuric acid increases with acid concentration, it should be possible to operate the scrubber at acid strengths above 80%. The 80% level was chosen because this is the optimum concentration for the standard Lead Chamber Process upon which the original work was based. In operating the isothermal scrubber in the Catalytic Chamber Process, the only limitation on the acid strength is that imposed by the sulfuric acid content of the exit gas at the operating temperature of the scrubber. As the acid concentration is increased, the operating temperature of the scrubber must be increased in order to maintain the vapor pressure of the water over the acid equal to the partial pressure of water in the entering gas. At some acid strength, the temperature reaches a level where the vapor pressure of sulfuric acid becomes high enough such that the effluent gas would contain an undesirable amount of sulfuric acid vapor. This condition is reached at an acid concentration of about 92% where the operating temperature of the scrubber would be about 400° F and the H_2SO_4

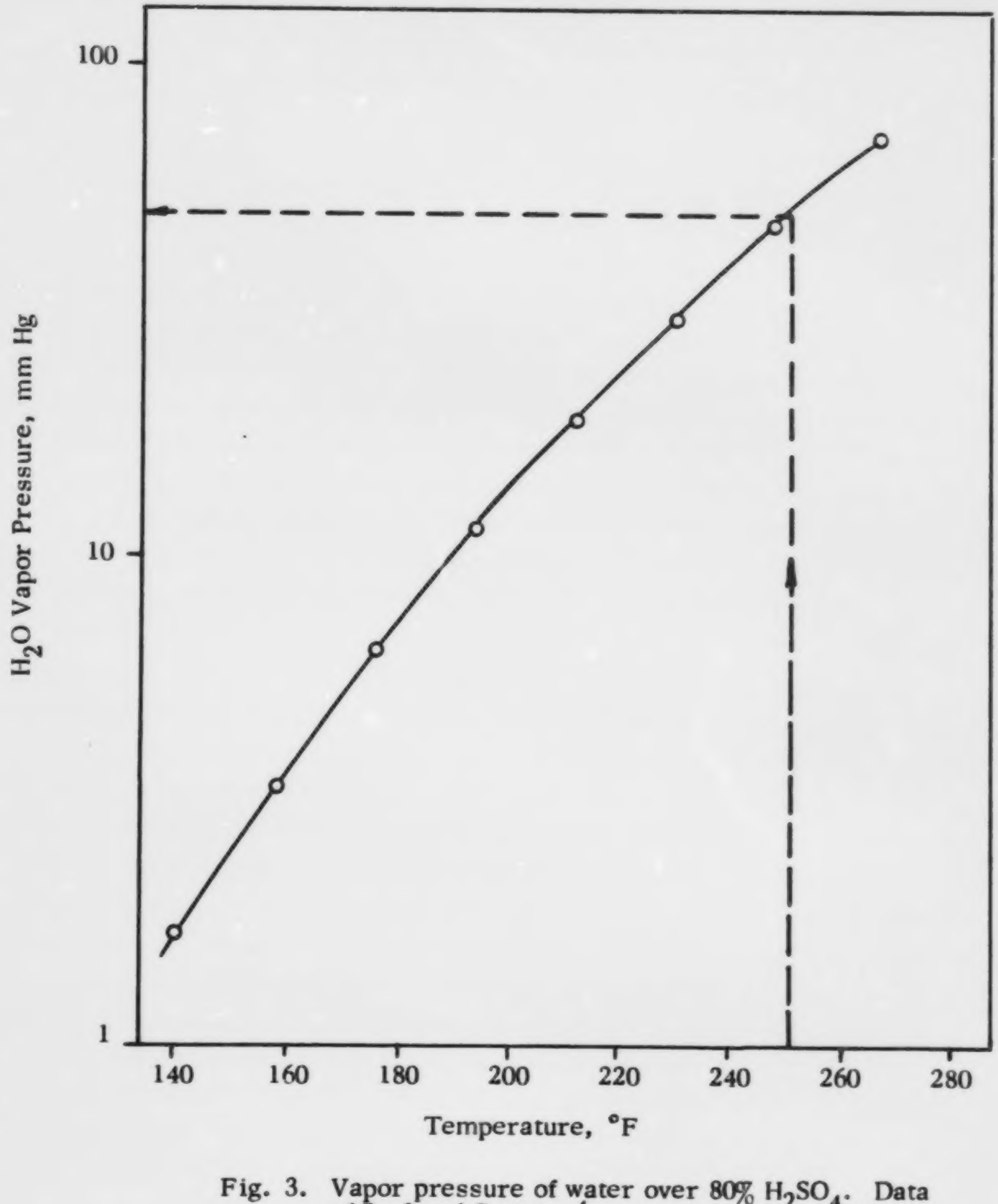


Fig. 3. Vapor pressure of water over 80% H_2SO_4. Data of Berl and Saenger [4]

vapor pressure is 1.9 mm Hg. A standard Chamber Plant could not operate at 93% acid because of the difficulty in recovering the oxides of nitrogen from a nitrose of greater than 80% sulfuric acid content. This limitation has been avoided by using a catalytic stripper as will be discussed in the next section.

F. Catalytic Stripper

The most critical part of the new process is the recovery and reoxidation of the oxides of nitrogen. In the standard Chamber Plant the nitrogen oxides are sufficiently concentrated that the reoxidation can occur simultaneously with the sulfur dioxide oxidation even though the reaction rate is comparatively show at the operating temperature use. Nitrogen oxide recovery is effected by the dilution and heating of the nitrose which causes an increase of the vapor pressure of the oxides which are then swept out of the acid by the high temperature gases from the sulfur burner. Both heating and diluting are impractical when treating dilute, wet flue gases in the Catalytic Chamber Plant because they involve a requirement for heat beyond that which enters the system with the flue gas. Heat balance calculations on such a system show that the heat penalty would be enormous; as much as 40% of the total heat generated by the power plant would be necessary.

The breakthrough that was achieved during this contract that avoids this heat penalty was the discovery that by contacting the nitrose with a catalyst such as activated charcoal in the presence of oxygen, the oxides of nitrogen are oxidized to nitrogen dioxide in the liquid phase and the NO_x is recovered quantitatively in a relatively small volume of carrier gas. Figure 4 shows a schematic diagram of the catalytic stripper that would be used to accomplish the nitrogen oxide recovery.

The exact mechanism of the oxidation reaction has not yet been determined, but the net effect is that the total nitrogen oxide content of the nitrose is converted to the relatively insoluble nitrogen dioxide which is spontaneously evolved from the sulfuric acid. No additional heat is required to drive the reaction to completion; as a matter of fact the overall process is somewhat exothermic. Details of the experimental verification of this oxidation can be found in Section V-K4c.

G. Nitric Acid Absorber

One of the major advantages of the Catalytic Chamber Process is that it provides for the recovery of nitrogen oxides that are formed during the combustion of coal in the power plant, thus eliminating another source of air

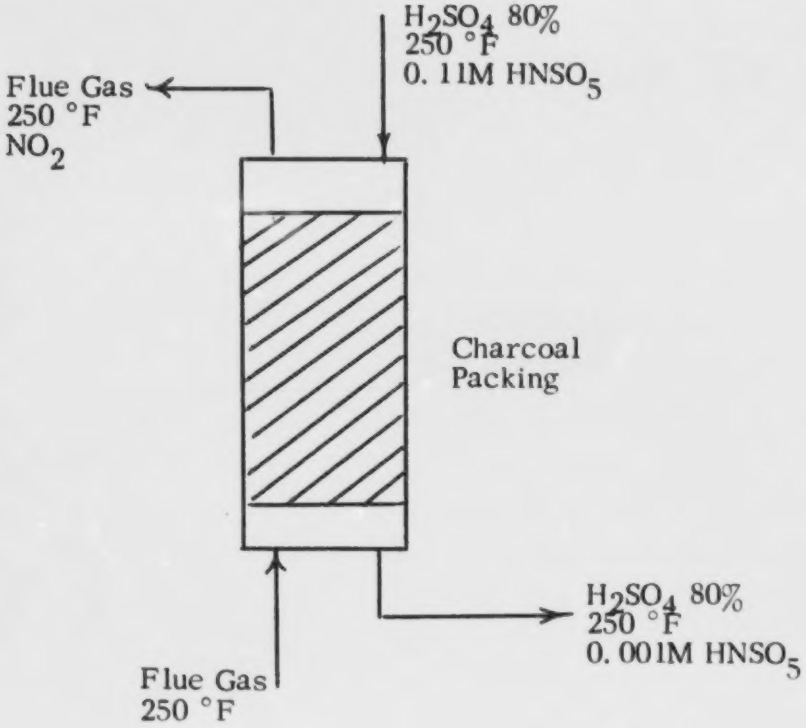

H_2SO_4 80%
250 °F
0.11M $HNSO_5$
Flue Gas
250 °F
NO_2
Charcoal
Packing
H_2SO_4 80%
250 °F
0.001M $HNSO_5$
Flue Gas
250 °F

Fig. 4. Catalytic Stripper

pollution. The oxides, which are primarily in the form of nitric oxide, mix with the recycle nitrogen dioxide and are scrubbed from the flue gas in the isothermal scrubber. Sufficient nitrogen dioxide must be provided to ensure that the ratio of nitric oxide to nitrogen dioxide is unity by the time the reacted gases reach the scrubber so that the total nitrogen oxide content can be absorbed in the sulfuric acid.

Thus, when the nitrogen oxides are recovered in the catalytic stripper, there is an excess in the recycle stream equal to the amount of nitrogen oxides recovered by the process. This excess NO_2 can be converted to **52%** nitric acid by scrubbing a sidestream of the stripper gas effluent with water according to the reaction:

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

Since the absorption of the nitrogen dioxide does not occur efficiently at high temperatures, the sidestream must be cooled to 100° F before it enters the scrubber. The nitric oxide in the carrier gas is returned to the incoming flue gas. Although some heat is lost in this process, the total volume of the sidestream is so low that this loss has little effect on the overall heat balance.

It is interesting to note that in general, power plants make a distinct effort to minimize the amount of nitrogen oxides being generated in the boiler in order to avoid pollution. As will be shown in more detail in a later section, the Catalytic Chamber Process, being designed to recover the nitrogen oxides in the flue gas as nitric acid, can be operated more profitably as the amount of nitrogen oxides in the stack gas increases. Discussions with two large power generating companies have shown that the oxide level can be increased substantially without any loss in power generating efficiency.

H. Process Economics

A preliminary economic analysis of the Catalytic Chamber Process has been performed based on guidelines established by the National Air Pollution Control Administration. This analysis is shown on the following pages in Tables III through VII and refers to a plant operated in conjunction with an 800 MW power plant producing 1.44 million SCFM of flue gas.

Table III. Estimated Major Equipment Cost*

Item	Function	No.	Size	Cost
1. Cyclone Separator	Remove coarse fly ash	3	487,000 cfm	245,000
2. Scrubber	Remove N_2O_3, H_2SO_4 and fly ash	3	35 ft. dia. 70 ft. high 8 ft/sec	$1,500,000
3. Stripper	Recover N_2O_3	2	32 ft. dia. 60 ft. high 2 ft/sec	250,000
4. HNO_3 Absorber	Recover NO_x at 52% HNO_3		44 ft. dia. 60 ft. high	450,000
5. Filter	Remove fly ash from acid	3	38,000 gal/min acid flow	250,000
6. Product Storage Tank	Store H_2SO_4	3	100,000 gal	100,000
7. Exhaust fan	Provide differential pressure	3	12" H_2O 87×10^6 SCFH	60,000
8. Gas Cooler	Cool stripper gas	1	2.5×10^6 BTU/hr 2100 feet square area	20,000
9. Gas Cooler	Cool reactor gas	6	124×10^6 BTU/hr 105,000 feet square area	525,000
10. Pumps	Move acid from scrubber to stripper	8	38,000 gal/min 60-ft head	50,000
11. Pumps	Move acid from stripper to scrubber	8	38,000 gal/min 70-ft head	50,000
				$3,500,000

---

* 800 megawatt (e) power plant producing 1.44×10^6 SCFM flue gas.

Table IV. Estimated Capital Cost Summary*

	Item	Factor
1.	Major Equipment (see Table III)	1.00
2.	Erection labor and foundation	.38
3.	Piping	.55
4.	Instruments	.05
5.	Insulation	.03
6.	Electrical	.05
7.	Building	.20
8.	Plant facilities	.05
9.	Plant utilities	.08
10.	Receiving, shipping, etc.	.05
11.	Physical Plant costs	2.44
12.	Engineering and Construction	.60
13.	Direct plant cost	3.04
14.	Contractor's fee	.10
15.	Contingency	.15
16.	Fixed capital costs	3.29

17. Total fixed capital costs = \$3,500,000 x 3.29 = \$11,515,000

---

* 800 megawatt (e) power plant producing 1.44 x 10^6 SCFM flue gas.

Table V. Annual Operating Costs*

Raw materials and chemicals	
Catalyst replacement	$500,000
Packing replacement	100,000
Water (3500 GPM at $0.10/M gal)	168,000
Direct labor	108,000
Supervision	27,600
Maintenance at 0.05 of fixed capital	653,000
Supplies at 15% of maintenance	98,000
Utilities	
Power	145,700
Heat	0 †
Total direct cost	$1,800,300
Payroll burden (20% of direct labor and supervision)	16,600
Plant overhead (50% of direct labor, supervision, maintenance, and supplies)	416,600
Packing and shipping	425,000
Waste disposal	25,000
Other	
Total indirect cost	$ 873,200
Depreciation (10% of fixed capital)**	1,151,500
Taxes (2% of fixed capital)	230,300
Insurance (1% of fixed capital)	115,150
Other	
Total fixed cost	$1,496,950
Total operating cost	$4,170,450 (or $1.64/ton of coal)

---

* 800-megawatt (e) power plant producing 1.44×10^6 SCFM flue gas. (Coal consumption = 2.22×10^6 tons/yr)

† Heat is needed only for start-up and process adjustment situations.

**10 year straight-line depreciation.

Table VI. Return on Investment
(Basis: 80% H_2SO_4, 600 ppm NO_x in Flue Gas)

Credits *		
H_2SO_4 at $20/ ton	$ 5,030,000	
HNO_3 at $40/ ton	1,100,000	
		6,130,000
Total Operating Cost		4,170,450
Net Operating Profit		$1,959,550
$/ ton coal †		$0.88
Return on Investment (before tax)		17%

---

* Production figures based on the material balance in Table I are

27,600 tons/yr HNO_3 (100%)
314,000 tons/yr H_2SO_4 (80%)
252,000 tons/yr H_2SO_4 (100%)

† Coal consumption = 2.22×10^6 tons/yr

Table VII. Return on Investment (Basis: 93% H_2SO_4, 2000 ppm NO_x in Flue Gas)

Credits*		
H_2SO_4 at $30/ton	$7,530,000	
HNO_3 at $40/ton	4,470,000	
		12,000,000
Total Operating Cost (including an additional 430,000 for heating the flue gas to 400° F to maintain 93% H_2SO_4 in scrubbing system)		4,600,000
Net Operating Profit		$ 7,400,000
$/ton coal		$3.34
Return on Investment (before taxes)		64%

*Based on: 252,000 tons/yr H_2SO_4 (100%)
112,000 tons/yr HNO_3 (100%)

Table III lists the Major Equipment Items and their cost. The estimated total is \$3.5 million. An item that was not included, but may be necessary is mist eliminators for the gas effluent from the scrubber. At this point it is not known if they will be necessary, so they will not be considered until more engineering data is available. Table IV shows the development of the equipment multiplier used to obtain the total fixed capital costs of \$11.5 million. These figures are also based on recommendations of NAPCA.

Table V is a breakdown of the estimated annual operating costs for the Catalytic Chamber Process. It is interesting to note the low cooling water cost and the complete absence of additional heat costs. These two items, which were major expenses in earlier versions of the process, have been completely eliminated due to the technological breakthroughs achieved in the Catalytic Chamber Process Concept.

Table VI presents the very attractive profitability picture for the process in Figure 1 having the feedstream described in Section IV B (0.3% SO_2; 600 ppm vol. NO_x). The assumption is made that 80% sulfuric acid can be sold at \$20 per ton (100% basis) and 52% nitric acid can be sold at \$40 per ton (100% basis). These numbers are reasonable in today's marketplace although they might not be if every coal burning power plant started producing acid. More will be said about this matter later.

If the plant is run at the highest possible acid concentration, 93%, a considerable price advantage should be realized. At current market prices 93% sulfuric acid should be worth \$30 per ton (100% basis), thus giving an increase in the revenue at very little cost. There would be a slight increase in operating cost because the gas would have to be heated to about 400° F to maintain the proper temperature in the isothermal acid loop. This would be partially offset by the fact that the cooling stages would no longer be necessary. In any case the fact that the acid is kept at one temperature keeps the additional heating cost at a very low level. The maximum that this heat would cost would be \$430,000 per year and this may be reduced by both the credit in savings on cooling water and any heat that could be recovered from the cleaned stack gases.

In addition, it has been found through discussions with two large power producers that it would take very little effort and would cost virtually nothing to supply a raw flue gas containing 2000 ppm of nitrogen oxides instead of the 600 ppm assumed for the economic analysis in Table VI. Therefore, at no additional cost more than three times as much nitric acid could be recovered for sale. An economic analysis was made based on both the sale of 93% sulfuric acid and the production of additional nitric acid, the return on investment would be 64% as shown in Table VII.

This number seems to be high, but it was calculated using the limits of the OAP guidelines for capital and operating costs. The only variable whose value is difficult to determine is the selling price of the acids. The factors that go into the evaluation of the market value of sulfuric and nitric acids produced from power plant stack gases are very complex and are beyond the scope of this contract. In addition, marketing factors should be taken into account: will power generating companies want to go into the chemical business? Should acid be manufactured if it has to be shipped fairly long distances to customer, etc? Some of these questions are discussed in the next section and make the picture a little more clear. The major point is that the Catalytic Chamber Process can be operated at a profit while purifying power plant stack gases to a highly acceptable level, so long as acid markets exist and remain intact over the life of this air pollution control equipment.

I. Effect on the Sulfuric Acid Industry

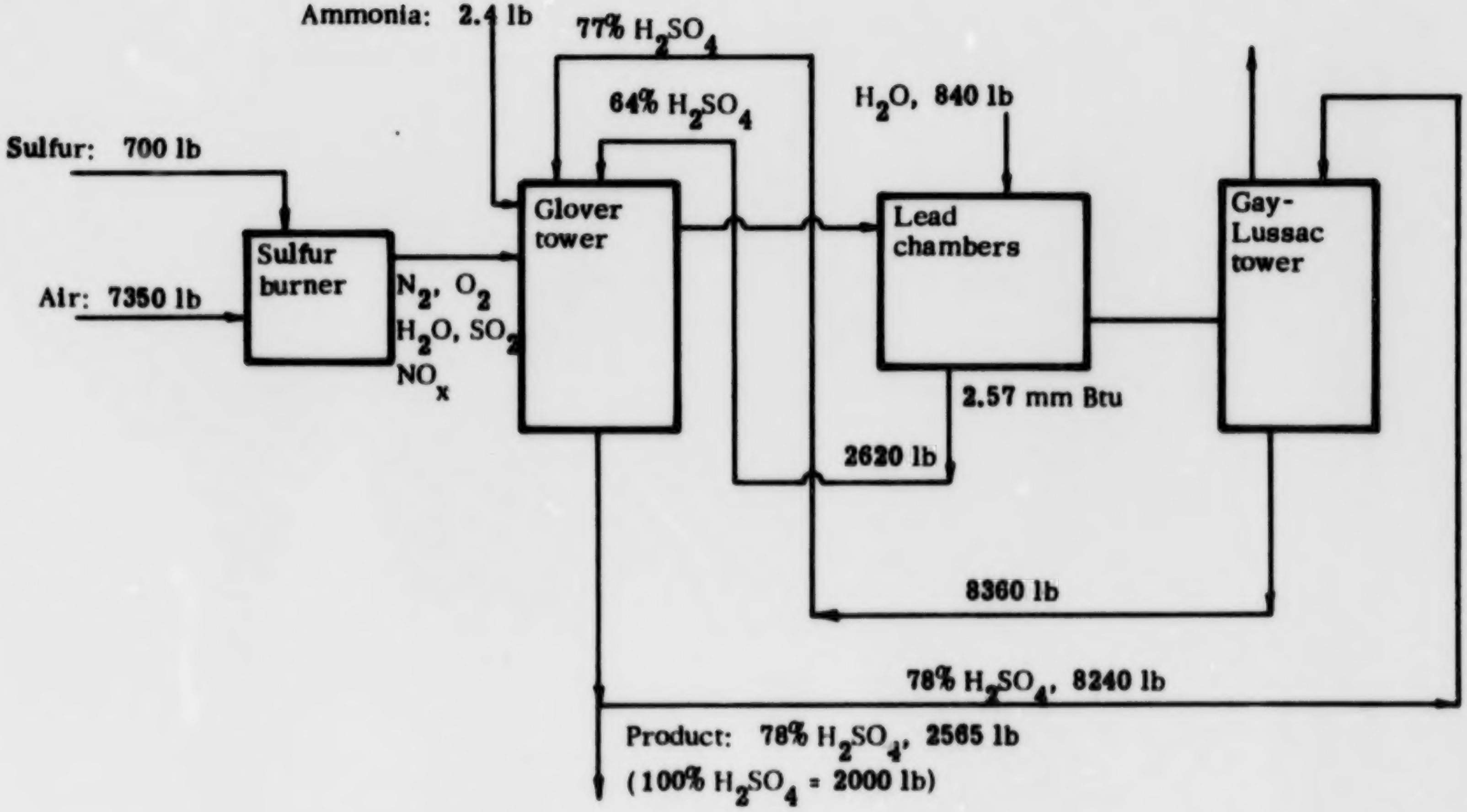
The Catalytic Chamber Process has the potential for profound effect on the sulfuric acid industry[5, 6] first through the increase in the overall production of acid if coal burning power plants use the process for pollution clean-up, and secondly because of the possibility of a new process for acid production from conventional sulfur sources. The problem is quite complex and a full treatment is beyond the scope of this report, but a few points should be made at this time.

From a technological viewpoint, the Catalytic Chamber Process could revive the concept of the Lead Chamber Process from its present obsolescence. There are two basic, interrelated reasons for this obsolescence: the conventional Chamber Process cannot economically produce acid stronger than about 77%, and conventional Chamber Plants cannot be built, as a practical matter, much larger than 100 tons per day.

Examination of the conventional process (see Figure 5) shows why these problems exist. The acid concentration is determined by the ease of recovering the nitrogen oxides from the scrubber acid in the Glover Tower (stripper). As the sulfuric acid concentration is increased, the nitrosylsulfuric acid (and thus the nitrogen oxides) becomes more soluble and the N_2O_3 vapor pressure at a given $HNSO_5$ concentration decreases. Above 77%, the heat required to denitrate the acid is greater than can be supplied by the hot gases from the sulfur burner, thus limiting the sulfuric acid concentration in the Glover Tower to this level.

The size limitation of the conventional process is based on both the large amount of heat generated during the sulfur dioxide oxidation and the slow reaction rate of nitric oxide oxidation. The gases in the chambers react in a relatively concentrated mixture so that a great deal of heat is given off due to the oxidation of SO_2. This heat must be dissipated in order to facilitate the reoxidation of the nitric oxide produced. The NO oxidation reaction has an inverse rate vs. temperature relationship; i.e., the higher the temperature, the lower the reaction rate. Since the rate of NO reoxidation is slow in any case (thus requiring long residence times), care must be taken to keep the temperature down to effect reoxidation as fast as possible. To remove the necessary amount of heat the chambers must have very large surface areas and to fully reoxidize the NO the chambers must provide large residence volumes, thus creating the requirement for huge box-like chambers. The necessary size of the chambers for a small plant is obtained from Fig. 52 in Appendix 3. The size of a conventional Chamber Plant producing 1000 tons/day (ten times the capacity of the standard Chamber Plant) staggers the imagination.

Most of the acid strength and size problems are avoided in the Catalytic Chamber Process. The nitrogen oxides are no longer recovered by heating the nitrose; instead the denitration is accomplished by catalytic oxidation of the nitrosylsulfuric acid at moderate temperatures. This means that no additional heat is needed for the stripping step and it will work as well with highly concentrated acid as with 77% acid. In addition, the 93% concentration limit placed on the flue gas clean-up process is not applicable to a process which treats a dry gas such as the off-gas from a sulfur burner, be-



Sulfur: 700 lb
Air: 7350 lb
Sulfur burner
Ammonia: 2.4 lb
N$_2$, O$_2$
H$_2$O, SO$_2$
NO$_x$
Glover tower
77% H$_2$SO$_4$
64% H$_2$SO$_4$
H$_2$O, 840 lb
Lead chambers
2.57 mm Btu
2620 lb
Gay-Lussac tower
8360 lb
78% H$_2$SO$_4$, 8240 lb
Product: 78% H$_2$SO$_4$, 2565 lb
(100% H$_2$SO$_4$ = 2000 lb)

Fig. 5. The Lead Chamber Process Flow Diagram*

cause there is no need to run the scrubber at high temperature conditions to avoid absorbing H_2O. The process would be water deficient so there would be no excess water to force through the scrubber and the whole process could be run at low temperatures. At low temperatures, there would thus be no problem with sulfuric acid vapors to keep the maximum concentration down.

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*From Duecker and West, 3rd ed., p 119.[7]

The size problem is considerably reduced in the Catalytic Chamber Process because there is no need to minimize the temperature in the chambers to accelerate the NO reoxidation reaction. In the new process the nitrogen oxide oxidation would take place separately in the catalytic stripper, so the emphasis on cooling the chambers is reduced. The SO_2 oxidation reaction rate is increased with increasing chamber temperatures making it even more attractive. There would still be the necessity to cool the gas at some point because the system would have excess heat, but this could be turned into an economic advantage. The gas from the sulfur burner enters the system at about 1600°F, thus being about 1300°F hotter than necessary. This is a very high grade heat source and could be easily adapted to electrical power generation to supply power to the plant complex.

These process considerations are in the conceptual stage of development, but the advantages to be derived from them cannot be overlooked. Future work should be devoted to examining the engineering aspects of the process to determine if the Lead Chamber Process can indeed make a come-back.

V. THE EVOLUTION OF THE CATALYTIC CHAMBER PROCESS: CONCEPTUALIZATION AND EXPERIMENTATION

A. General

This section of the report will follow the step-by-step development of the Catalytic Chamber Process from the concept presented in the original proposal through the experimentation, concept reformulation, pilot plant design and construction, heat and material balances and economic analysis which led to the current process as outlined in Section IV. The approach will be chronologically oriented rather than divided into process stages. This is intended to show the evolution of the process as a whole rather than the development of individual unit operations.

B. The Originally Proposed Concept

As originally proposed, the Tyco process for flue gas clean-up was essentially the Lead Chamber Process with only minor modification, as can be seen from Figure 6. The distillation column is equivalent to the Chamber Process' Glover Tower and the packed bed collector is the Gay-Lussac Tower, with only the acid filtration step and the acid collection technique being new to the process. At that time, there was no provision for recovering nitric acid from the process.

In the originally proposed Chamber Process for stack gas clean-up, the flue gas at 900°F enters the distillation column where it contacts a recycle stream of sulfuric acid containing dissolved oxides of nitrogen and excess water. The hot gas concentrates the acid and recovers the oxides of nitrogen for sulfur dioxide oxidation. The gas mixture continues on to the retention chamber which provides the residence volume to enable the SO_2 oxidation to occur:

$$SO_2 + NO_2 \rightarrow SO_3 + NO$$

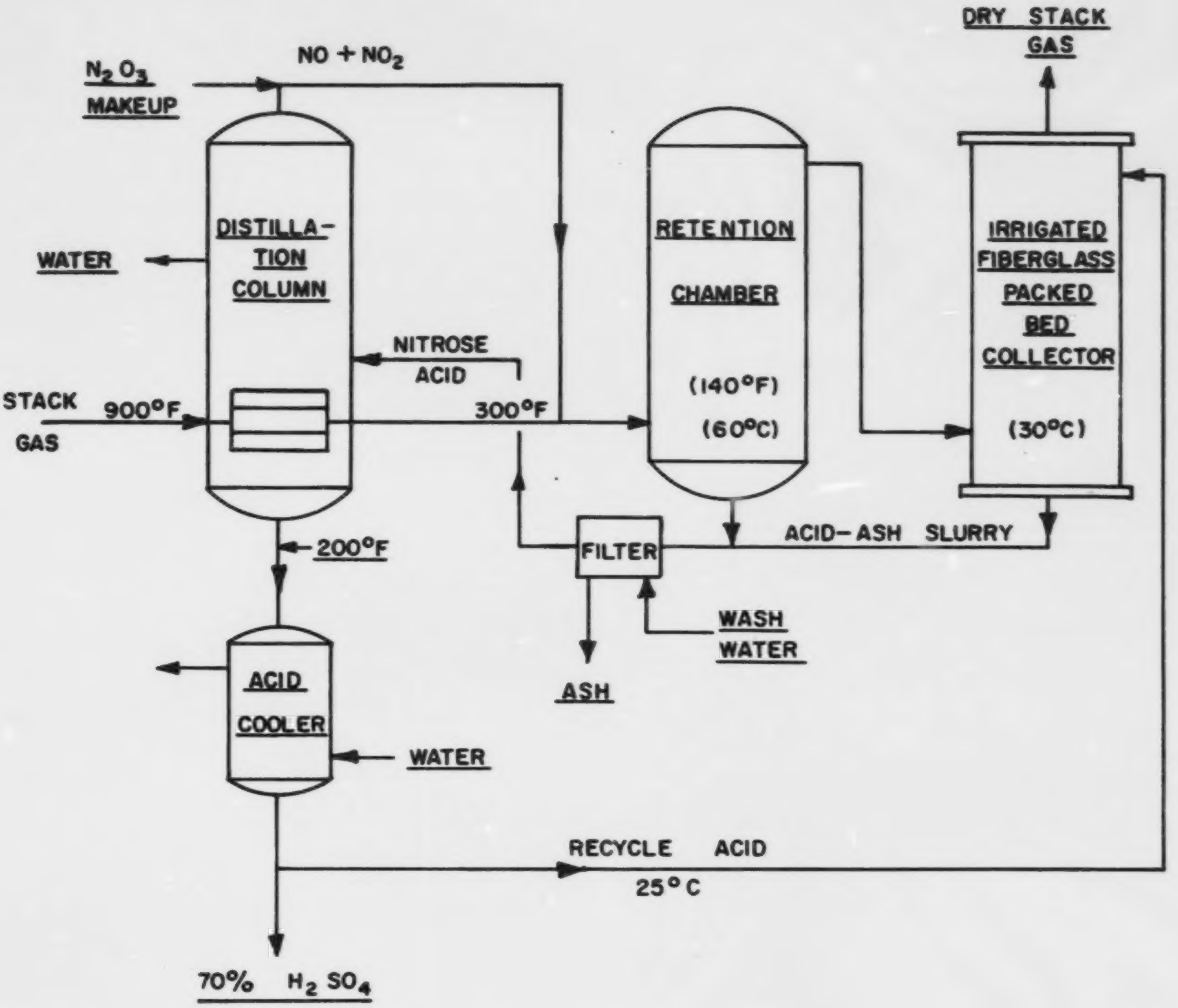

DRY STACK GAS
NO + NO2
N2 O3 MAKEUP
DISTILLATION COLUMN
WATER
NITROSE ACID
STACK GAS
900°F
300°F
RETENTION CHAMBER
(140°F)
(60°C)
IRRIGATED FIBERGLASS PACKED BED COLLECTOR
(30°C)
200°F
FILTER
ACID-ASH SLURRY
WASH WATER
ASH
ACID COOLER
WATER
RECYCLE ACID
25° C
70% H2 SO4

Fig. 6. Originally Proposed NO_2-Oxidation Process for Recovery of SO_2 from Power Plant Stack Gas

The SO_3 interacts with the water in the gas stream to form sulfuric acid mist which remains entrained in the gas. In addition the retention chamber provides the volume for the reoxidation of NO to NO_2 :

$$2\,NO + O_2 \rightarrow 2\,NO_2$$

The NO which is formed during the SO_2 oxidation must be reoxidized in this system before it enters the scrubber/collector in order to allow recovery of the oxides. Both nitric oxide and nitrogen dioxide are relatively insoluble in sulfuric acid separately, but when present in equimolar amounts they are soluble up to 60% by weight through the formation of nitrosylsulfuric acid:

$$NO + NO_2 + 2\,H_2SO_4 \rightarrow 2\,HNSO_5 + H_2O$$

Therefore, the mole ratio of NO to NO_2 must be accurately maintained at unity in order to efficiently scrub the nitrogen oxides from the gas stream.

The sulfuric acid mist, the oxides of nitrogen and the entrained fly ash in the flue gas are scrubbed out of the gas stream with clean, cool sulfuric acid in the fiberglass packed-bed collector. The clean, dry gas is then vented to the atmosphere. The collector has to be packed with fiberglass in a fashion similar to a commercial mist collector in order to achieve maximum recovery of the sulfuric acid mist, a notably difficult material to remove from gas streams.

The nitrose from the collector is filtered to remove the fly ash and is then passed through the distillation column for recovery and recycle of the nitrogen oxides. In addition, the hot gases vaporize the excess water that was picked up in the scrubber so that the acid leaving the distillation column is both free of the oxides of nitrogen and is of the desired concentration. Product acid is drawn off from this stream after being cooled and the remainder is recycled to the collector.

C. Feasibility of Original Concept

It was well known that the nitrogen dioxide oxidation of sulfur dioxide was a feasible technique as evidenced by the long standing success of the Lead Chamber Process for sulfuric acid manufacture. What remained to be determined was whether the technique would work with a wet, dilute flue gas as well as with the dry, concentrated product of a sulfur burner. Table VIII summarizes the differences between the two gases.

TABLE VIII. Comparative Characteristics of Power Plant Flue Gas and Sulfur Burner Gas (Lead Chamber Process)

	Flue Gas	Sulfur Burner Gas
Temperature (°F)	300	1600
Sulfur Dioxide Concentration (%)	0.3	10-13
Water: SO_2 Ratio	**24:1**	1:15

1) Temperature. The Lead Chamber Process requires a hot (1600°F) gas in order to concentrate the acid and vaporize the oxides of nitrogen in the Glover Tower. With flue gas being available at only 300°F, could the proposed process operate at some reasonably economical level considering the heat that would have to be put into the system? This could be determined only after the process had been worked out in some detail and complete material and heat balances were developed, after which an economic analysis could be made.

2) Gas Concentration. The reaction kinetics of the Lead Chamber Process have been worked out in some detail during the century or so that the process has been used for acid manufacture,[7,8] and it was well known that the limiting reaction was the slow reoxidation of the nitric oxide in the lead chambers. However, virtually nothing had been done at the low sulfur dioxide levels present in flue gases. What remained to be done was to determine if the sulfur dioxide could be oxidized at relatively high rates at 0.3% concentration and if the resulting nitric oxide could be oxidized back to nitrogen dioxide within a reasonably sized reactor.

3) Water Content. The lead Chamber Process requires that water be added to it because the feed gas contains only about 1/15 of the water needed to make sulfuric acid from the sulfur dioxide. The power plant flue gas, on the other hand, contains more than 20 times too much water for acid production so some technique must be employed to remove water from the system. The question was: can this be done economically?

These three points were the basic questions that had to be answered before any scale-up could be attempted. There were other problems that also had to be analyzed before the feasibility of the process could be determined. Among these were:

- Maximum SO_2 recovery efficiency
- Maximum nitrogen oxide recovery efficiency
- Operating temperatures of the scrubber, reaction chamber and stripper
- Optimum product acid concentration
- Effect of fly ash on product acid purity
- Liquid and gas phase analytical techniques

D. Batch Kinetic Study

In order to evaluate the effect of low sulfur dioxide concentrations in the flue gas a series of kinetic studies were initiated using the batch reactor shown in Fig. 7. Concentrations of reactants (NO_2 and SO_2) were measured spectroscopically in the ultraviolet range as a function of time, the amount of NO_2 being determined by the fractional extinction at 5100 Å and the SO_2 obtained from that at 2560 Å. Later in the program techniques were developed using the infrared region of the absorption spectra which permitted more complete gas analysis at no loss in accuracy. The details of the UV analytical procedure can be found in Appendix 1 and the procedures for the IR technique in Appendix 2.

As shown in Fig. 7 gases were expanded from three known volumes simultaneously into the water-jacketed UV absorption cell via a 4-way stopcock, all bores of which were of equal diameter and volume. One line contained $SO_2 + N_2$, a second $NO + N_2$, and the third $NO_2 + O_2 + N_2$. The N_2 was used as an inert additive to adjust the pressures of all three gas mixtures to 760 torr prior to expansion into the evacuated cell. Each of the gas mixtures was prepared by expansion of pure gases into a calibrated 500 cc bulb, adding N_2 to atmospheric pressure and allowing several hours for gas mixing. The volumes of burettes were about 25 cc each, and all three sections were of the same diameter tubing. However, expansion into the cell was carried out with the storage bulbs open to their respective burettes so that pressure drops due to expansion would be negligible. New gas mixtures were prepared for each run.

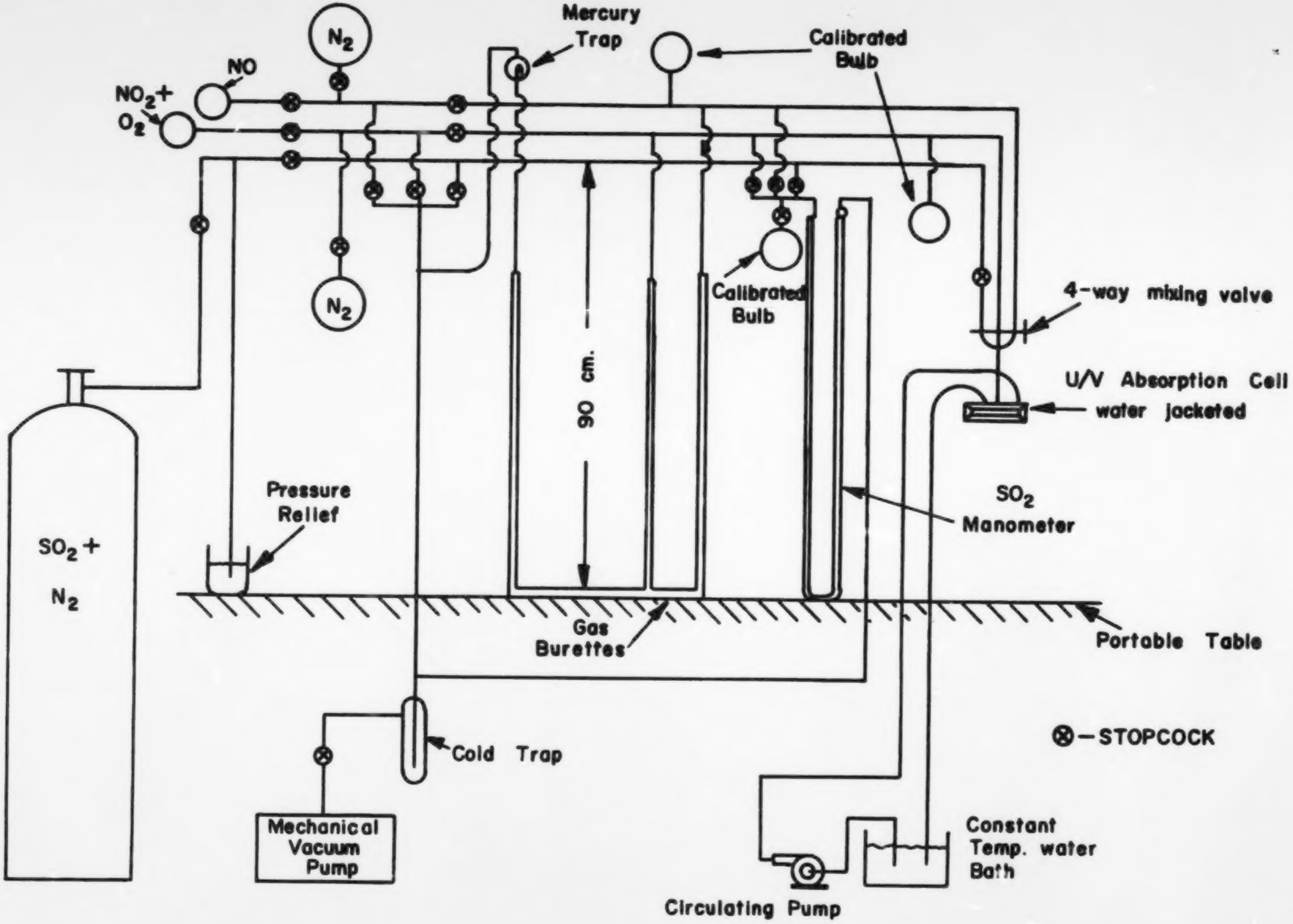

Mercury Trap
Calibrated Bulb
N_2
NO
NO_2 + O_2
N_2
Calibrated Bulb
4-way mixing valve
U/V Absorption Cell water jacketed
90 cm.
SO_2 Manometer
Pressure Relief
SO_2 + N_2
Gas Burettes
Portable Table
Cold Trap
⊗ – STOPCOCK
Mechanical Vacuum Pump
Constant Temp. water Bath
Circulating Pump

Fig. 2 Apparatus for measuring rate of oxidation of SO_2 by NO_2, and of NO by O_2.

To evaluate the response and mixing times in the apparatus, a test run was made with two of the lines filled with air and the third with a mixture of 33% NO_2 , balance O_2 . Simultaneous expansion into the evacuated cell resulted in a state wherein equilibration occurred within five seconds (see Fig. 8). The pressure of NO_2 in the cell using the spectroscopic measurement agreed with that predicted from the known system volumes.

In the experiments reported, the cell was first filled with 24 torr of water vapor (no liquid phase was initially present in the cell), prior to simultaneous expansion of the three gas mixtures into it. A few runs made with 150 torr H_2O vapor present in the cell indicated that the oxidation rate difference attributable to high water vapor concentrations is negligible.

Following these calibration tests, reactions between NO_2 and SO_2 were performed in the batch reactor apparatus. The conditions and results of these runs are listed in Table IX.

As can be seen from the results (Table IX and Figs. 9 and 10), the rate of SO_2 oxidation appears very much faster than that of the reoxidation of NO. Figure 11 clearly shows a dependence of rate on the square of the NO concentration, as would be expected. The effect of temperature on reaction rate for the NO reoxidation step is clearly shown in Fig. 10. The rate can be seen to decrease by about a factor of two for a 70 °C temperature rise under test conditions. This observation agrees well with data previously published.[9, 10] An inspection of Fig. 9 also shows that the initial concentration of NO_2 present seems to have little if any effect on the rate. The overall SO_2 oxidation rate, within the limits of pressures employed in this study, is controlled by the NO reoxidation time.

To insure that the product formed was actually H_2SO_4 and not some other species, an experiment was performed using a large bulb (1100 ml volume), with initial pressures of 2.1 mm SO_2 , 22 mm NO , 22 mm O_2 , 24 mm H_2O , and the balance nitrogen. After contacting the mixture, the bulb was rinsed several times with water and analyzed for sulfate by the barium nitrate gravimetric method. The ashed barium sulfate precipitate weighed 27.50 mg; theory, for the pressure of SO_2 used, is 29.30 mg. A quantity of sulfuric acid equal to 94% of theory was thus found. A duplicate run performed later using the same

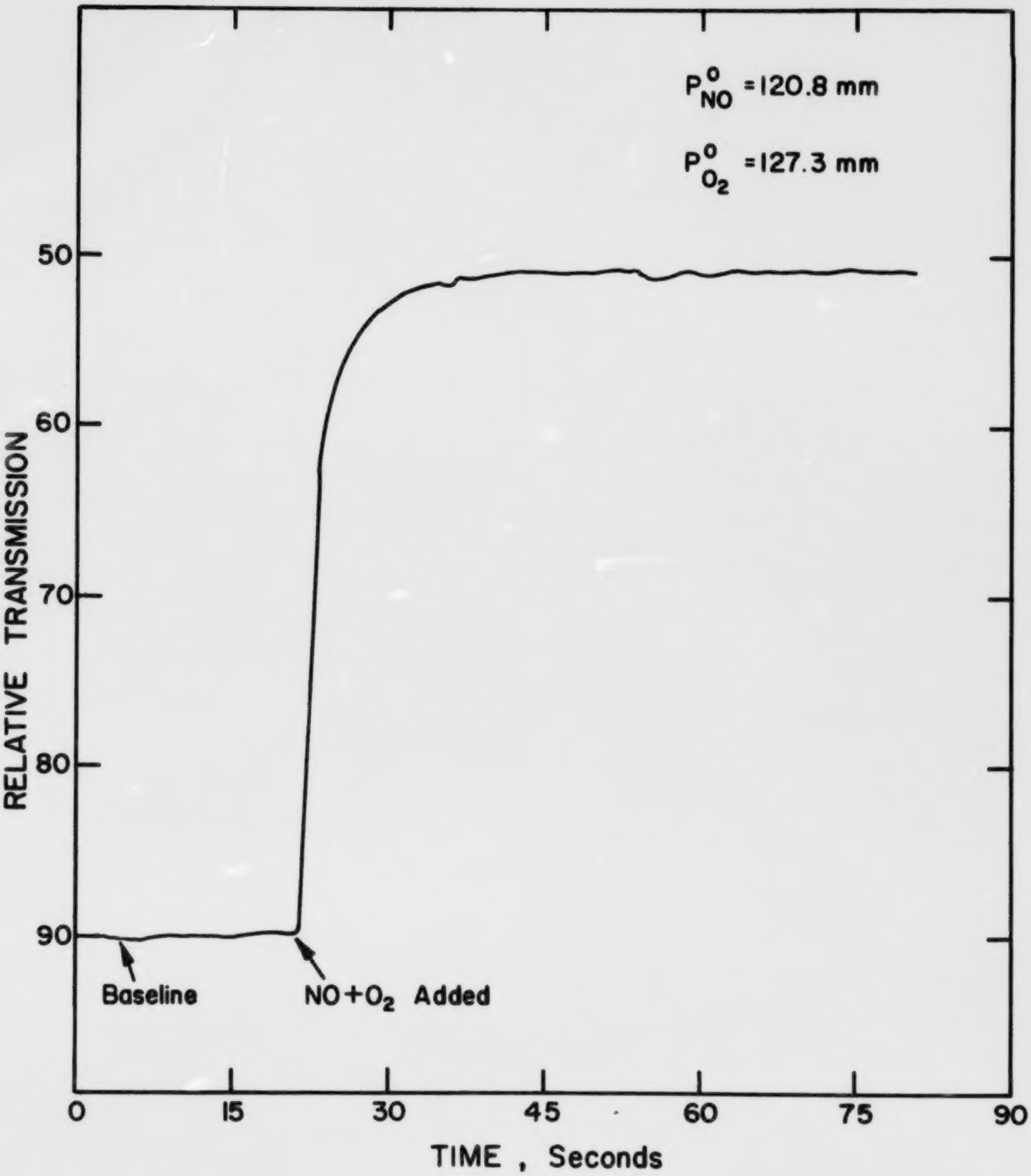


Fig. 8 Oxidation of NO by O_2 - 420 mμ.

TABLE IX

Rate of Oxidation of SO_2 by NO_2 (Batch tests)

	Initial Partial Pressures, mm Hg(3)						Reaction Time (Secs)	
Run No.	O_2	SO_2	NO	NO_2	H_2O	Temp. °C	SO_2(1)	NO_2(2)
1	21.6	6.4	16.7	10.8	24	56	84	282
2	56	4.2	62	28	24	56	22	26
3	20.0	2.3	21.5	21.5	24	56	~5	23
4	20.0	2.3	33.5	10.8	24	56	<5	<5
5	20.5	20.5	33.5	10.8	24	56	--	>300
6	20.0	2.3	33.5	10.8	24	56	<5	<5
7	21.0	2.6	30.4	32.2	24	56	<5	<5
8	20.0	2.3	11.0	33.9	24	57	<5	38
9	20.0	2.3	12.0	34.0	24	57	<5	43
10	20	2.1	10.5	10.5	24	56	<5	40
11	20	2.1	10.5	10.5	24	56	<5	41
12	20	2.1	10.5	10.5	24	56	<5	40
13	20	2.2	7.15	7.15	24	56	~5	50
14	20	2.2	7.05	7.05	24	56	~5	48
15	20.5	2.2	23.3	10.7	24	56	<5	17
16	20.5	2.2	23.3	10.7	24	56	<5	14
17	20	2.2	23.0	10.7	24	127	<5	30
18	20	2.2	23.0	10.7	24	127	<5	31
19	20	2.2	23	10.7	24	90	<5	27
20	20	2.2	23	10.7	24	90	<5	21.3
21	20	2.2	23	10.7	24	90	<5	27
22	20.4	2.2	21.1	21.4	24	56	<5	14
23	20.4	2.2	21.1	21.4	24	56	<5	16

---

(1) Time to reduce SO_2 to 10% of initial concentration.

(2) Time to return NO_2 to initial concentration.

(3) Balance of mixture N_2, total pressure 1 atm.

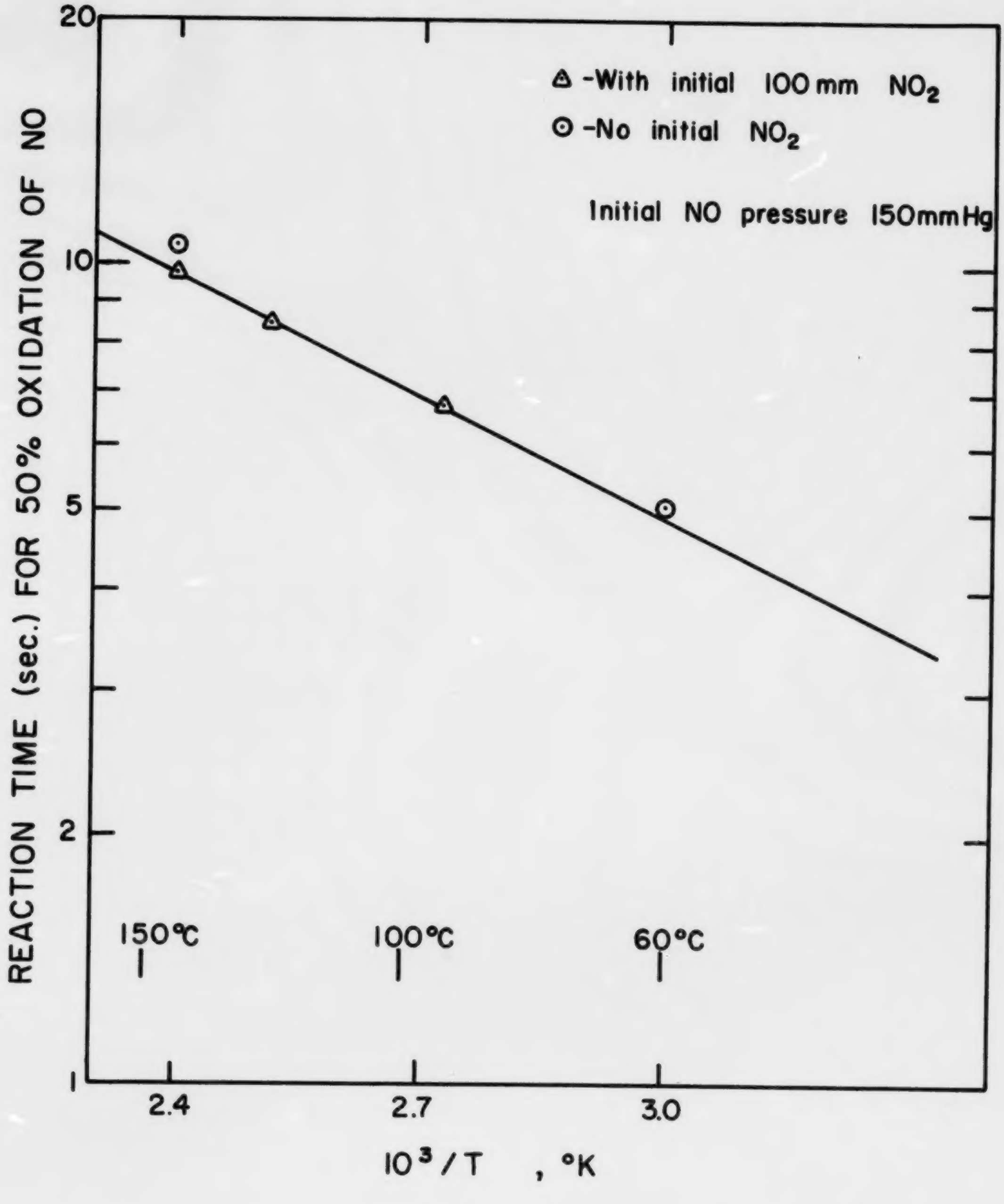


Fig. 9. Effect of NO_2 on the oxidation rate of NO.

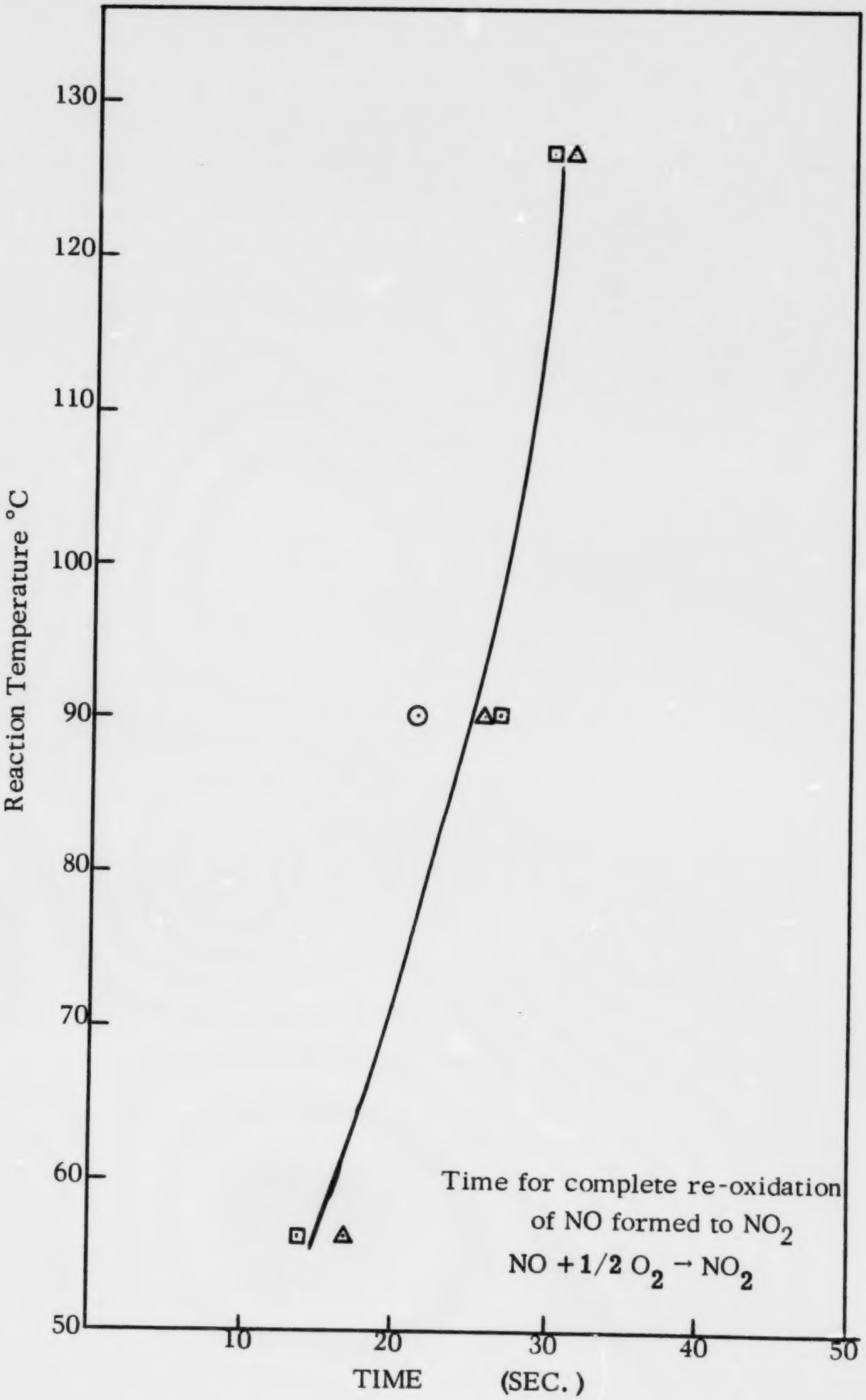


Fig. 10. Effect of temperature on the NO oxidation rate

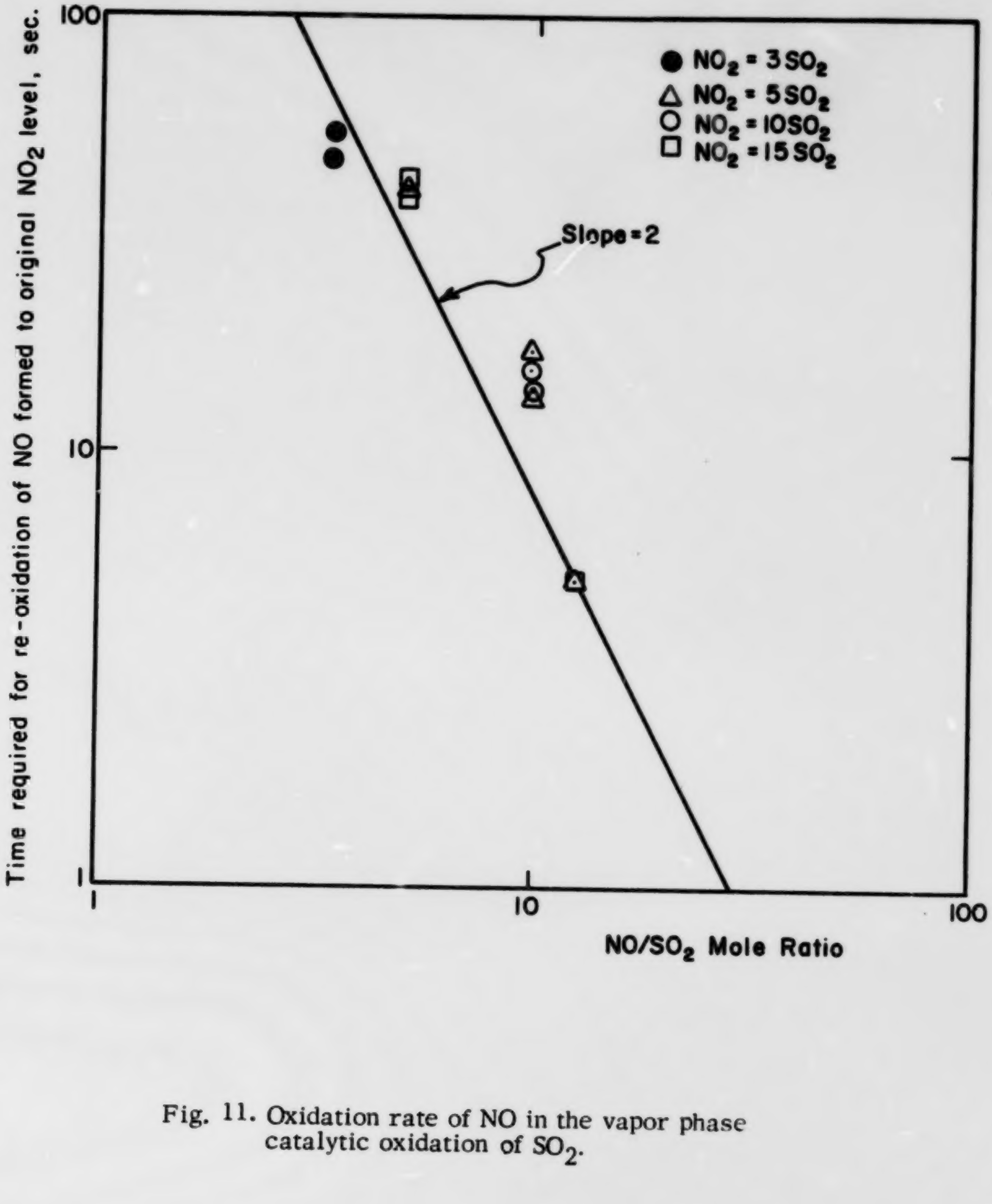


Fig. 11. Oxidation rate of NO in the vapor phase catalytic oxidation of SO_2.

procedure yielded 31.4 mg (again the theoretical yield was 29.3 mg). The averaged results of the two determinations show essentially 100% conversion of SO_2 to sulfuric acid, and it can be concluded that the reactions which occur are as have been postulated.

It can be seen from this experimentation that there is no problem in obtaining rapid oxidation of SO_2 with NO_2, but the simultaneous reoxidation of NO back to NO_2 is far too slow to be performed in this manner. The next section shows further experimentation designed to examine ways to improve this situation.

E. Nitric Oxide Oxidation

It can be shown that only two variables affect the oxidation of nitric oxide to nitrogen dioxide: temperature and nitric oxide concentration. It was determined experimentally that NO_2 concentration has no substantial effect (see Figs. 9 and 11) and it was shown previously that the concentration of SO_2 has a similar ineffectiveness.

From the reaction equation ($2\,NO + O_2 \rightarrow 2\,NO_2$) one would expect that the reaction rate would be proportional to the square of the nitric oxide concentration and directly proportional to the oxygen concentration. From this assumption, Burdick[11] has developed the following reaction rate equation which has been found to agree quite closely with experimental evidence.

$$Kt = \frac{1}{2\,Co - C_1}\left[\frac{1}{C} - \frac{1}{C_1}\right] - \frac{2.3}{(2\,Co - C_1)^2}\log\frac{(2\,Co - C_1 + C)(C_1)}{2\,CoC_1}$$

where:

K = Reaction rate constant
C = Concentration of NO at time t
Co = Original concentration of O_2
C_1 = Original concentration of NO

From this it would appear that the nitric oxide reaction rate could be increased by increasing the oxygen concentration, but as a practical matter this cannot be done. The oxygen content of the gas mixtures is determined by the source of the flue gas and would be very difficult to change. In addition, increasing the oxygen content would slightly decrease the nitric oxide concentration which has been shown to have far greater importance.

Burdick also found that the water content of the gas has an effect on the reaction rate. Very dry gases react about ten times as fast as mixtures with small amounts of water vapor, but beyond this small amount increasing water content has no effect. It is clear, therefore, that this factor, too, can be ignored since it would be impossible to completely dry the gas before the reaction took place. The variables that should be examined, therefore, are reaction temperature and NO concentration.

Figure 12 is a plot of the equilibrium constant, K_p , in the nitric oxide oxidation reaction as a function of temperature, calculated from handbook free energy data. It points out the somewhat unusual inverse temperature relation where the reaction rate decreases as the temperature increases. It is to be noted that below 300°F (425°K), the temperature of the flue gas entering the process, K_p exceeds 10^7 . This indicates that at this condition the equilibrium is highly favorable to oxidation of NO to NO_2 . This was verified experimentally as shown in Fig. 13 (see below for experimental technique). There is obviously a decided advantage to keeping the NO oxidation temperature well below 300°F.

A study of the external reoxidation of NO to NO_2 was made using the small-scale continuous kinetic apparatus shown schematically in Fig. 14. The same spectroscopic method of determining NO_2 concentrations as used before was employed, but with a cell of much shorter path length. Calibration curves at 5100 Å showed that at this path length the UV absorption method was reproducible and sensitive up to ca 300 torr. The effect of initial NO concentration was evaluated with the dependent variable being the rate of conversion of NO to NO_2 . The same procedures were used to determine the effect of NO_2 concentration and temperature as given in Figs. 12 and 13.

As shown in Fig. 15, the rate of oxidation of NO to NO_2 can be markedly increased when the reaction is catalyzed with coconut charcoal.

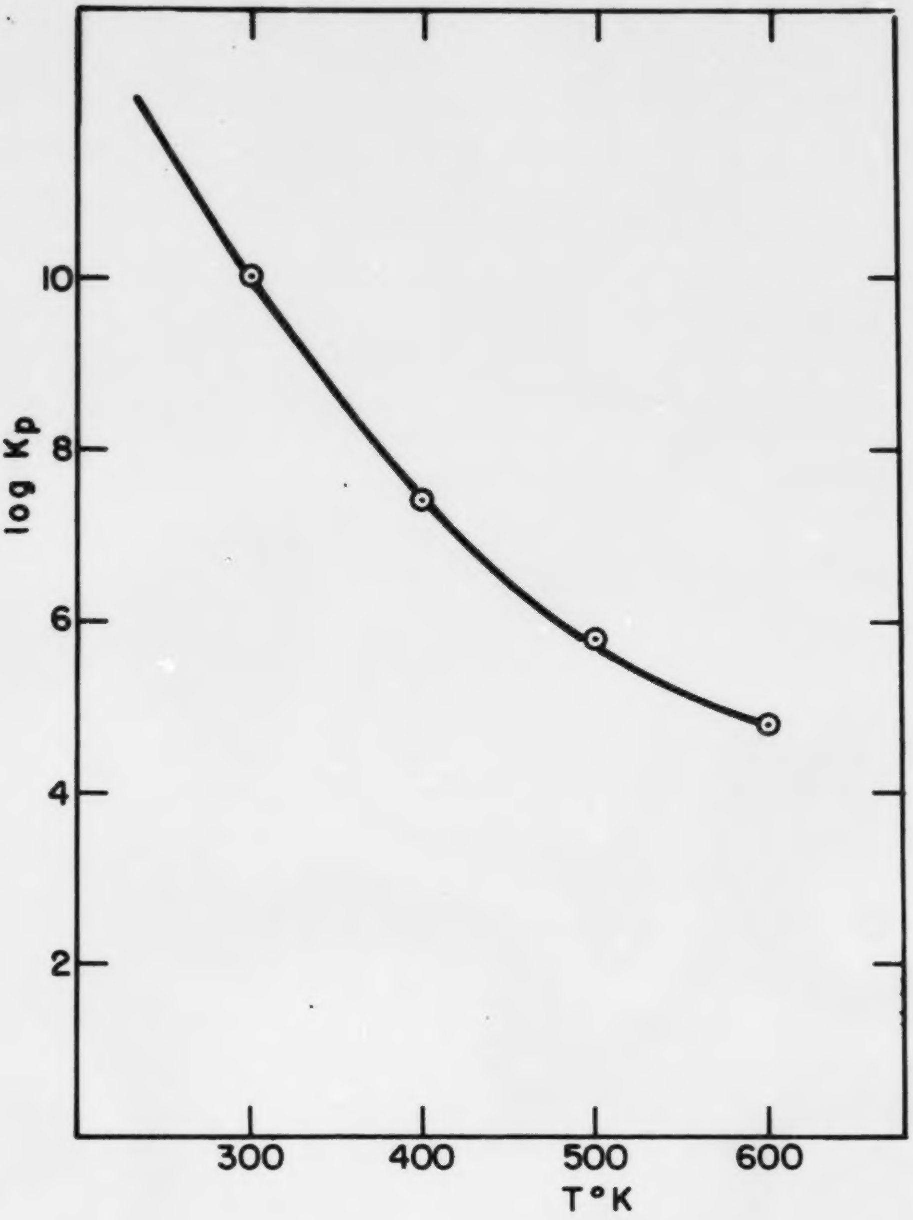


Fig. 12. Equilibrium constant in the reaction $2\ NO + O_2 \rightleftharpoons 2\ NO_2$ vs. temperature. (Stoichiometric reactant concentrations, 1 atm. total pressure.)

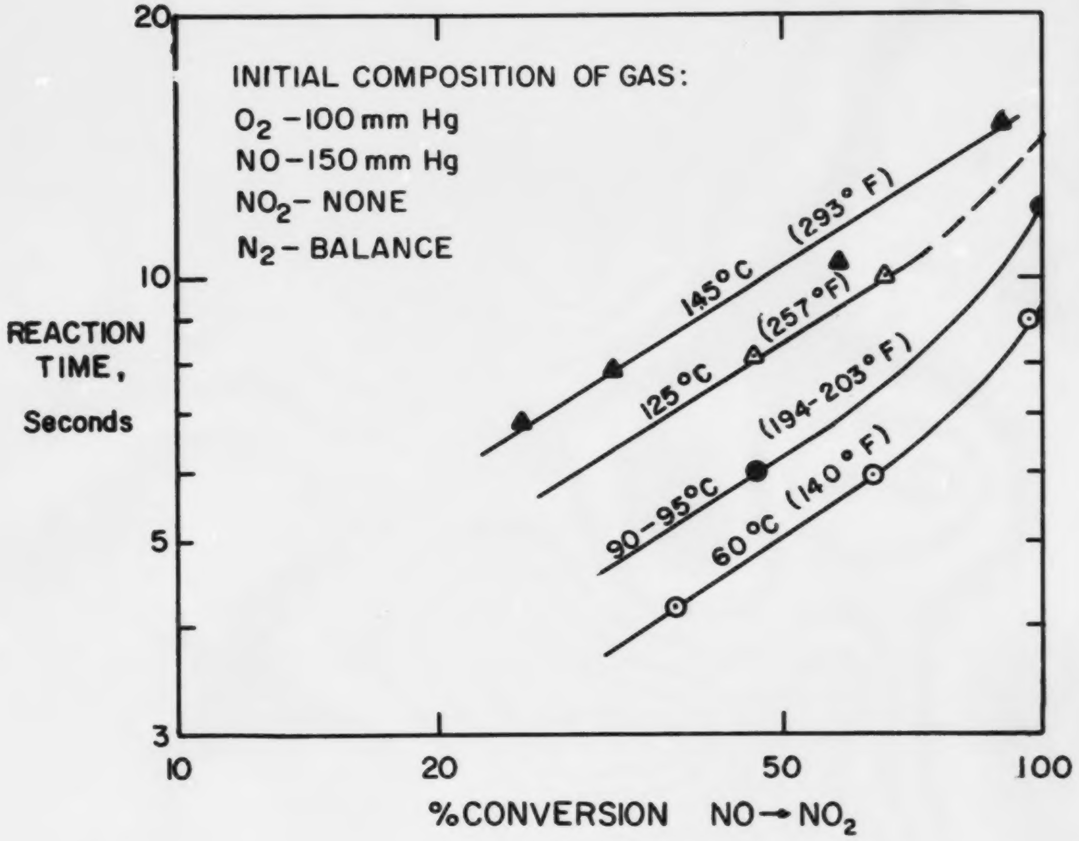


Fig. 13. Conversion rate of NO to NO_2 as a function of temperature.

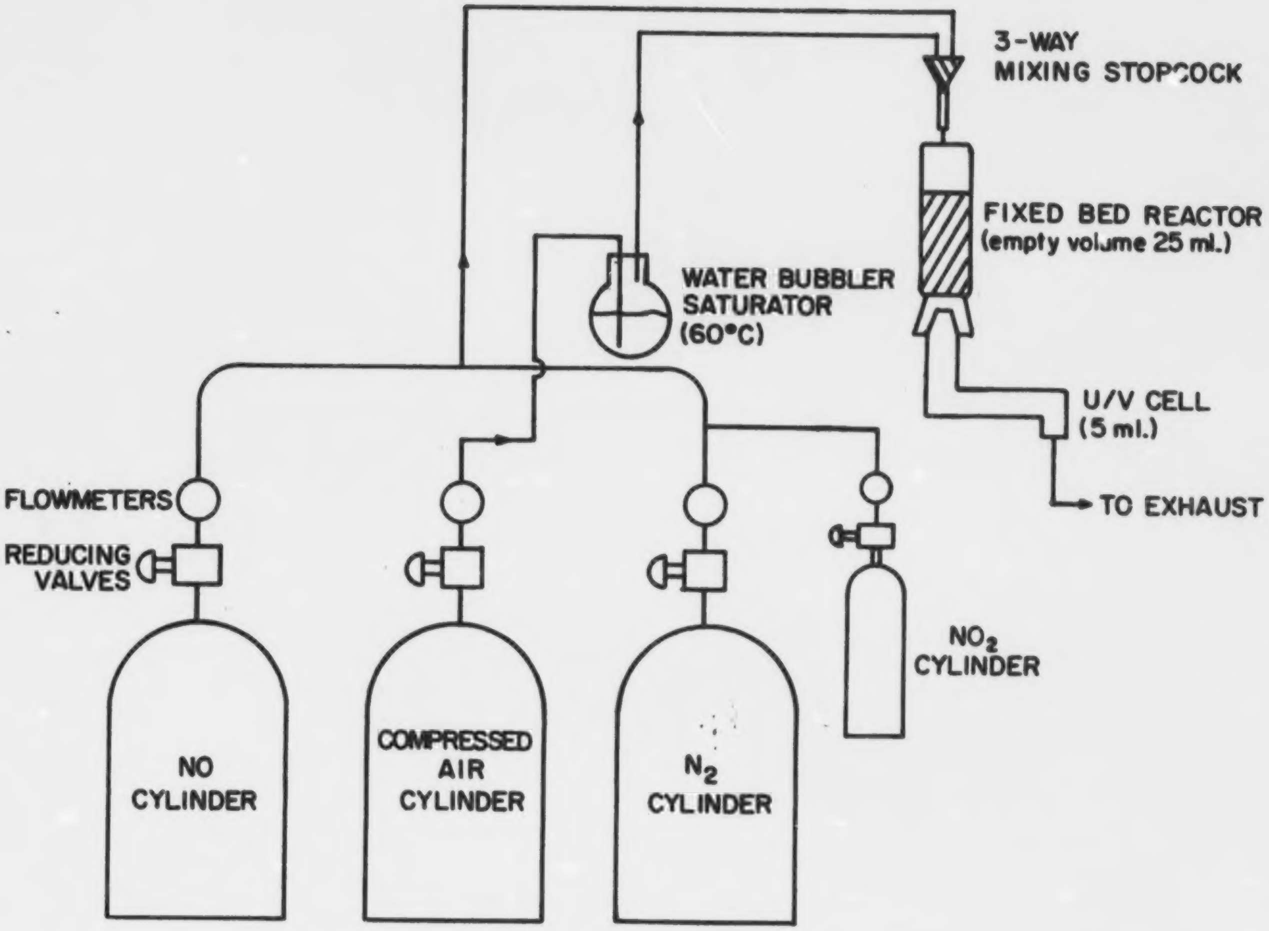

3-WAY
MIXING STOPCOCK
FIXED BED REACTOR
(empty volume 25 ml.)
WATER BUBBLER
SATURATOR
(60°C)
U/V CELL
(5 ml.)
TO EXHAUST
FLOWMETERS
REDUCING
VALVES
NO
CYLINDER
COMPRESSED
AIR
CYLINDER
N2
CYLINDER
NO2
CYLINDER

Fig. 14. Apparatus for Continuous Oxidation of NO to NO_2

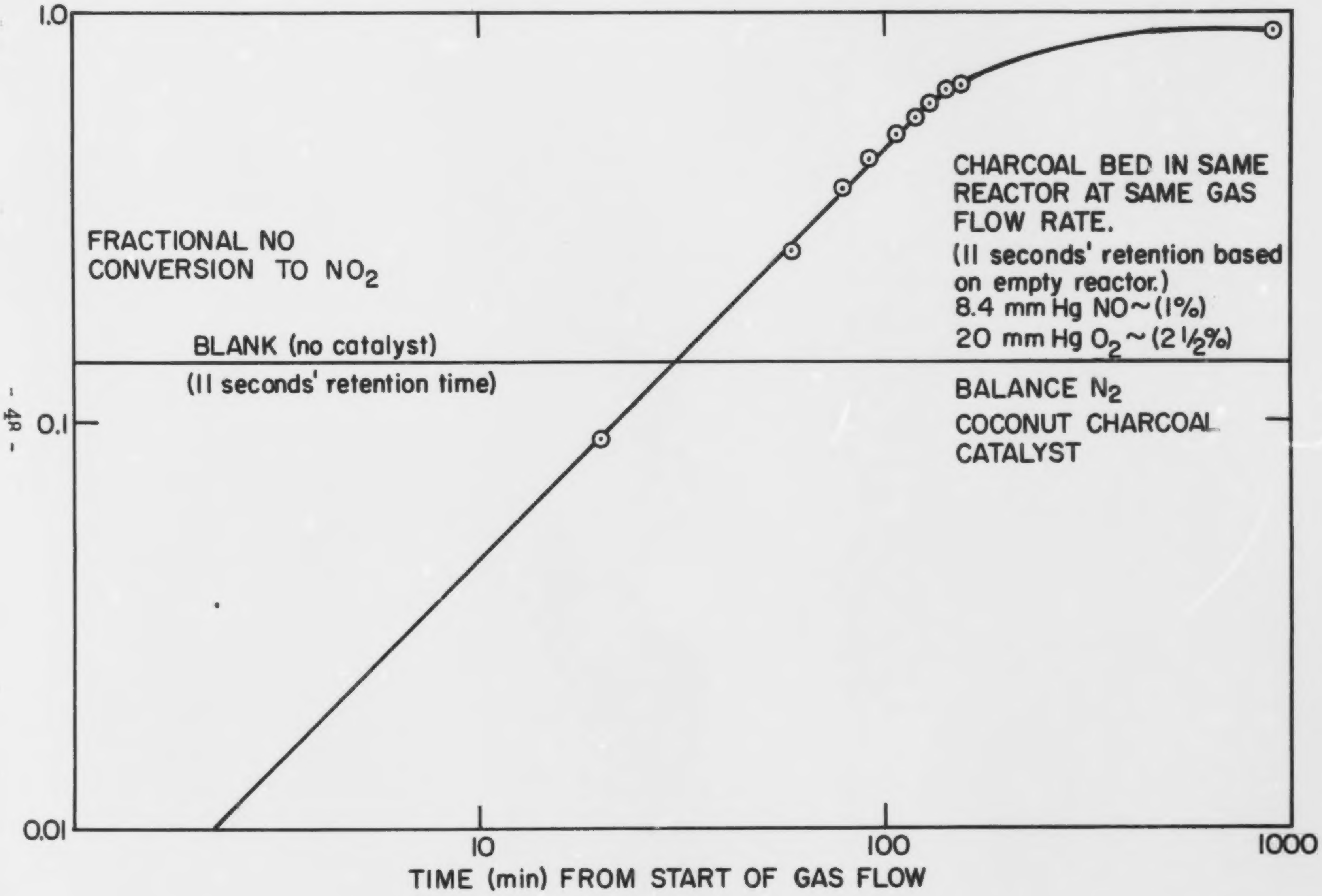


Fig. 15. Rate of Oxidation of NO to NO_2 using Charcoal Catalysis

As presented in Figs. ~~16 and~~ 17, at an initial concentration of 105 mm O_2, 135 ~~150~~ mm NO , 355 mm N_2 , and 150 mm H_2O , 85% oxidation of the NO to NO_2 was accomplished in 9 seconds' retention.

The results of the batch reactor study previously described indicate that with contact time of 1 - 2 seconds at least 90% of the SO_2 in flue gas can be converted to H_2SO_4 . The longer times needed to reconvert low concentrations of NO to NO_2 can be avoided by carrying out this step separately at higher concentrations and then feeding this gas (as a 3:1 molar NO_2/NO mixture) into the flue gas stream. After SO_2 oxidation, a 1:1 NO/NO_2 ratio will exist. This mixture (N_2O_3) can then be scrubbed, together with the sulfuric acid mist, from the flue gas stream in a packed bed collector unit. The N_2O_3 would then be recovered from the acid, thus creating a concentrated NO mixture which could be easily oxidized to NO_2 before being recycled. This scheme for separate NO oxidation will be shown in a later section describing the second generation Modified Chamber Process for SO_2 Removal from Power Plant Stack Gases.

F. Collection of Nitrogen Oxides and Acid Mist

The vapor phase catalytic process for SO_2 oxidation with NO_2 depends for its effectiveness on efficient (> 99.9%) collection of particulate matter and nitrogen oxide vapors. This was to be done using a stream of recycled sulfuric acid as the collection medium in a packed bed collection apparatus surmounted by a fiberglas mist collector of commercial design. To evaluate this aspect of the process, the apparatus shown in Fig. 18 was constructed. A laboratory-scale high efficiency flat bed mist collection unit and its associated feed tank were procured from Monsanto Co., manufacturers of commercial-scale fiberglas bed mist collection equipment. The unit, which has a gas flow capacity of about 1 cfm, was fed as shown, and its collection efficiency for both nitrogen oxides and particulate matter determined. The variables studied included the effects of gas velocity, pressure drop, gas composition and acid recycle rate.

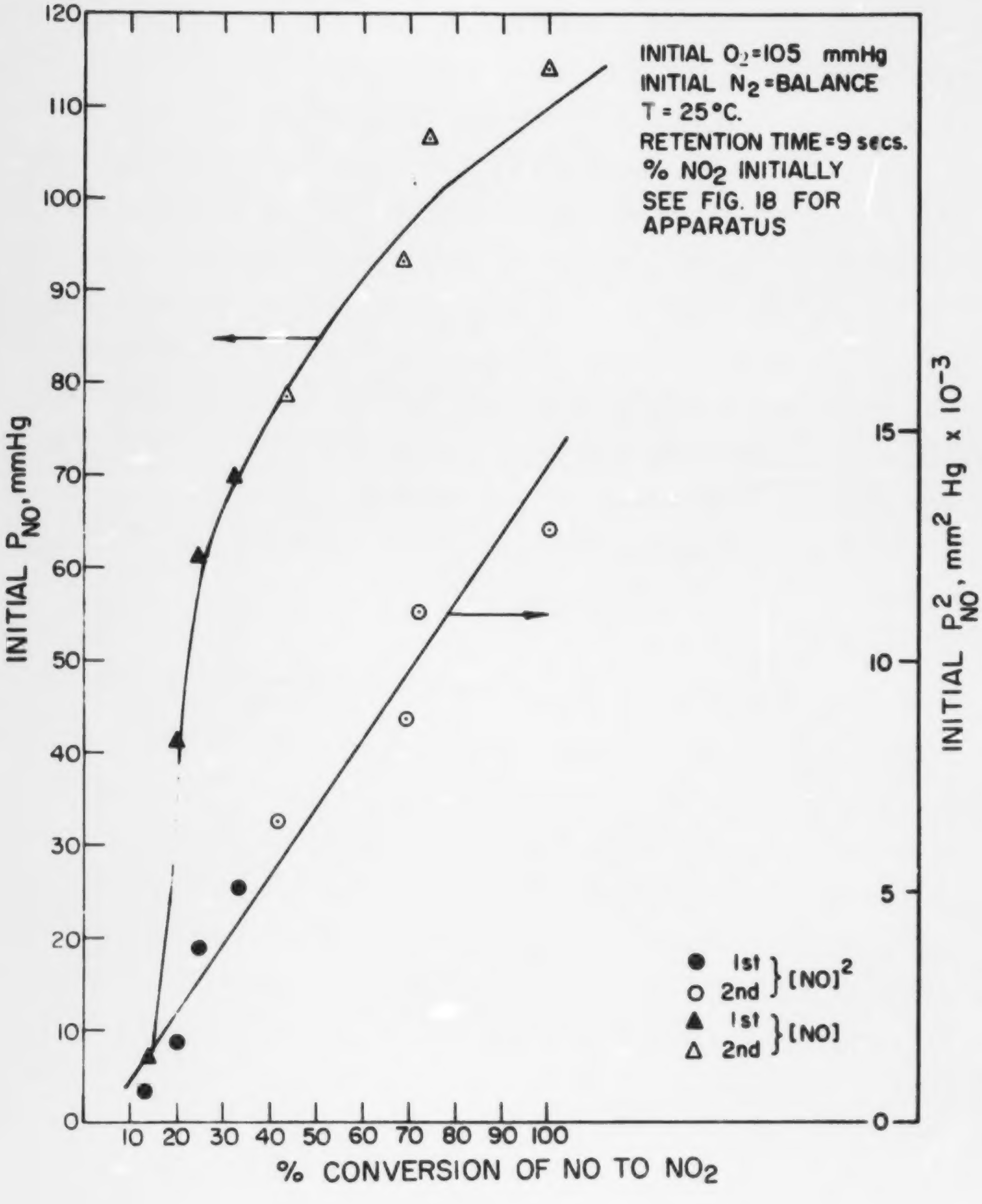


Fig. 16. Oxidation rate of NO at high NO concentrations without catalyst.

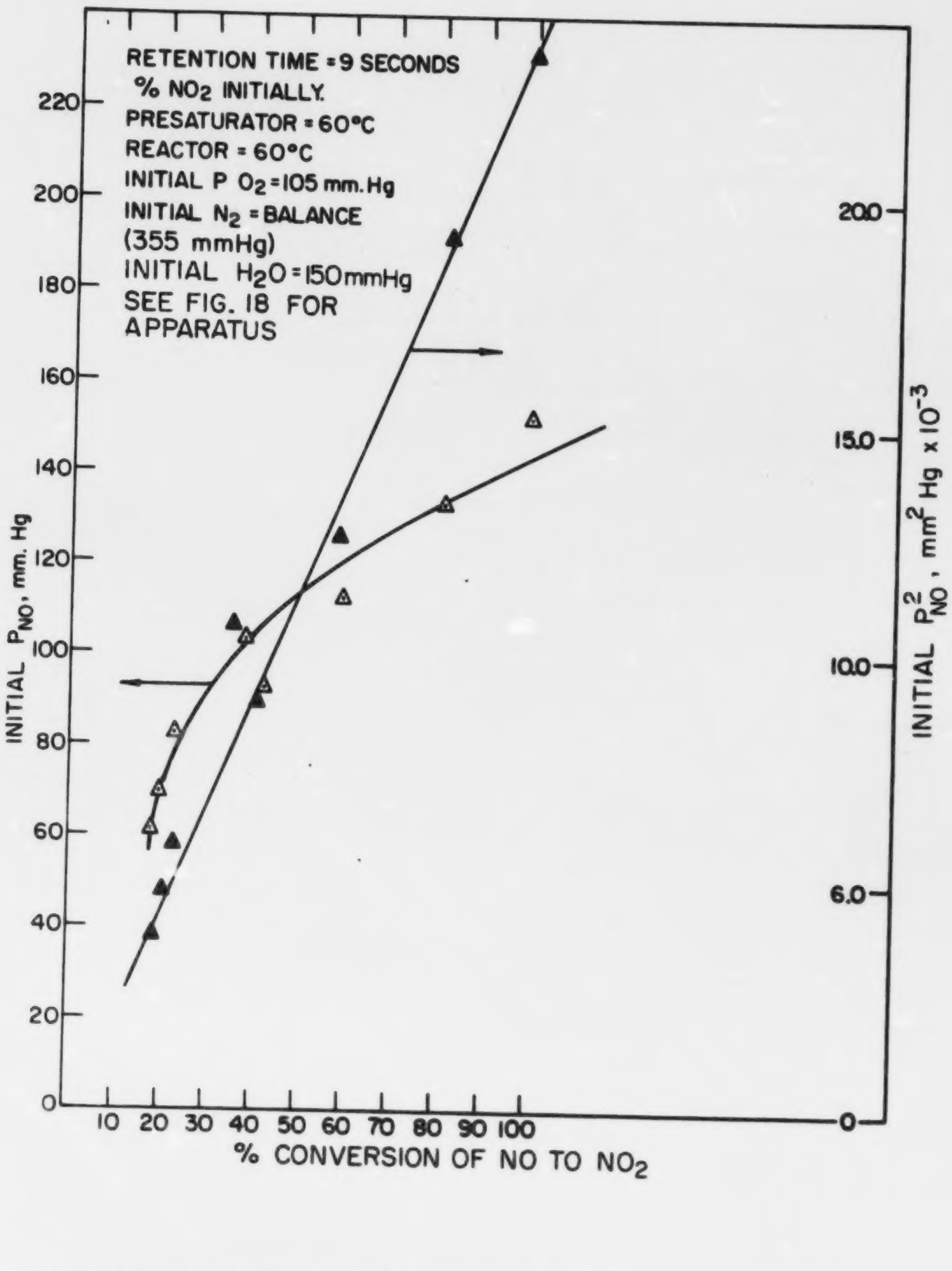


Fig. 17. Oxidation rate of NO at high NO concentrations without catalyst, 60°C

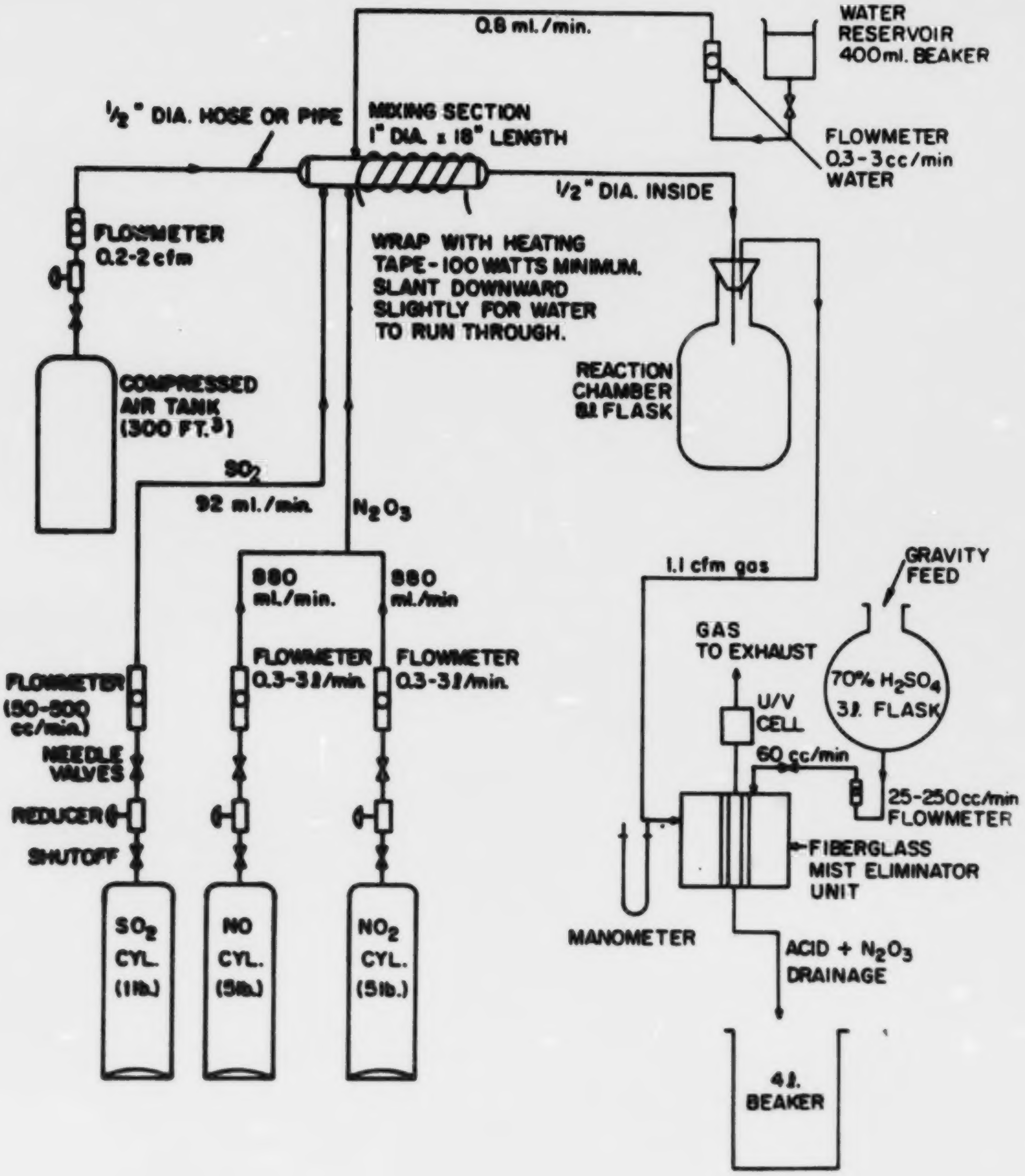

0.8 ml./min.
WATER RESERVOIR 400 ml. BEAKER
1/2" DIA. HOSE OR PIPE
MIXING SECTION 1" DIA. x 18" LENGTH
FLOWMETER 0.3-3 cc/min WATER
1/2" DIA. INSIDE
FLOWMETER 0.2-2 cfm
WRAP WITH HEATING TAPE-100 WATTS MINIMUM. SLANT DOWNWARD SLIGHTLY FOR WATER TO RUN THROUGH.
REACTION CHAMBER 8 l FLASK
COMPRESSED AIR TANK (300 FT.³)
SO₂
92 ml./min.
N₂O₃
1.1 cfm gas
GRAVITY FEED
880 ml./min.
880 ml./min
GAS TO EXHAUST
FLOWMETER 0.3-3 l/min.
FLOWMETER 0.3-3 l/min.
70% H₂SO₄ 3 l. FLASK
FLOWMETER (50-500 cc/min.)
U/V CELL
60 cc/min
NEEDLE VALVES
25-250 cc/min FLOWMETER
REDUCER
FIBERGLASS MIST ELIMINATOR UNIT
SHUTOFF
MANOMETER
ACID + N₂O₃ DRAINAGE
SO₂ CYL. (1 lb.)
NO CYL. (5 lb.)
NO₂ CYL. (5 lb.)
4 l. BEAKER

Fig. 18. Mist collection study apparatus flow diagram

After calibration of the flowmeter and UV cell, using a 6-inch path length cell, several experiments were made using this apparatus. In two initial runs, 20 cfh each of NO and NO_2, 1.5 cfm of air, 90 cc/min of SO_2 and 0.3 cc/min of liquid water were introduced into the flow reactor. The mist collector had H_2SO_4 flowing through the bed at a rate of 60 cc/min.

For a pressure drop of 35 inches of water, an NO_2 removal efficiency of 91.3% was found. Reduction of the pressure drop to 20 inches of water reduced the efficiency of NO_2 collection to 76%. Removal of the SO_2 was found to be essentially 100% in both cases.

Within the reactor, formation of a small amount of white crystalline material was noted. From its properties this material appears to be nitrosylsulfuric acid (SO_5NH).

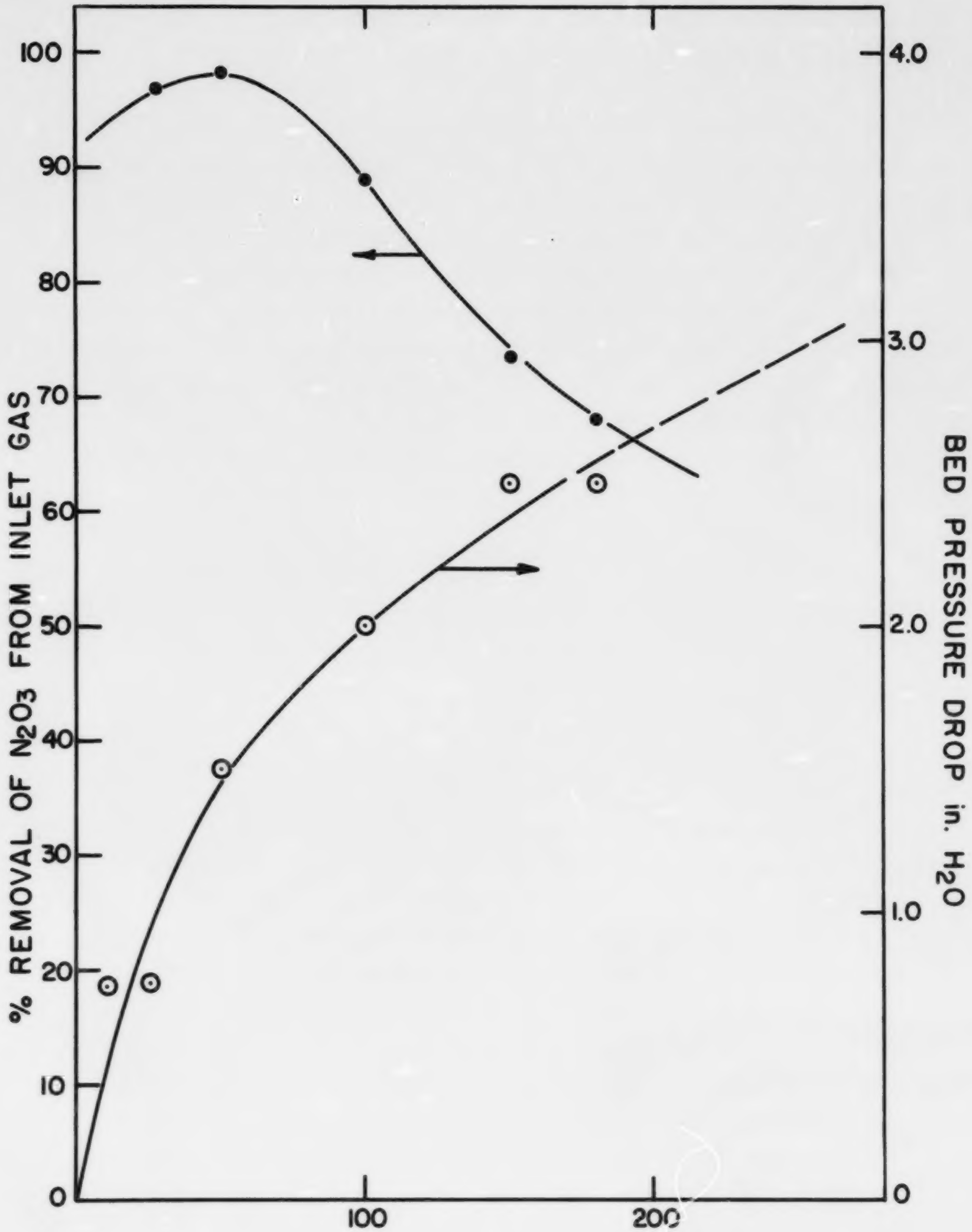
A second series of runs was conducted. For these, the following flow rates were used in all cases:

Air	21,600 cc/min of gas	(0.75 cfm)
NO_2	278 cc/min of gas	(1.3 volume %)
NO	62 cc/min of gas	(0.3 volume %)
SO_2	130 cc/min of gas	(0.6 volume %)
H_2O	0.3 cc/min of liquid	(1.7 volume %)

The H_2SO_4 flow rate through the mist collector was then varied, with values of 10 cc/min to 180 cc/min being studied. The results for NO_2 collection efficiency and pressure drop as a function of acid (70% H_2SO_4) flow rate are shown in Fig. 19. Fresh acid was used for each determination. For the same gas flow rates, the pressure drop across the mist collector bed tended to increase as the acid flow rate increased.

From the above results, it can be seen that at higher acid flow rates, flooding of the pores of the packing apparently reduces the amount of gas liquid interfacial area present at which absorption of the NO_2 can occur. At lower flow rates, however, insufficient acid is probably moving through the bed to take up all of the NO_2.

These preliminary results show that even with only a single absorption stage, N_2O_3 is scrubbed from the gas stream at high efficiency. While a countercurrent column scrubber is evidently required to attain the necessary 99.9^+% N_2O_3 collection efficiency, the number of stages needed should not be excessive.



H_2SO_4 FLOW IN FIBERGLASS BED, ml/min

Fig. 19. Collection efficiency for N_2O_3 and pressure drop across fiber mist collector unit.

G. Solubility of NO , NO_2 and Fly Ash in H_2SO_4

Data were collected on the solubility of NO and NO_2 in sulfuric acid as a function of acid concentration and temperature. Since the process depends for its effectiveness on efficient removal of oxides of nitrogen by scrubbing the effluent gas stream with recycled sulfuric acid, this solubility information is essential.

The solubility of NO in 74% sulfuric acid containing dissolved N_2O_3 is given in Table X below.

TABLE X Solubility of NO in 74% H_2SO_4 Containing SO_5NH(2)

Solvent	NO Absorbed					
	ml/ml Solvent		Solvent,	NO_2,	Total NO,	NO ~~CO~~/NO_2 ratio,
% N_2O_3	40°C	70°C	g/ℓ, 40°C	g/ℓ, 40°C	g/ℓ, 40°C	mol/mol, 40°C
1.18	1.47	1.61	1.72	11.7	9.4	1.23
4.3	6.40	6.20	7.48	42.6	35.4	1.27
1.11	2.85	2.93	3.33	11.0	10.5	1.46
3.86	10.10	10.20	11.8	38.2	36.8	1.48

These data are shown graphically in Fig. 20 and are compared with a theoretical line for pure nitrosylsulfuric acid. The curve from the data in Table X shows that the nitric oxide is not sufficiently soluble in the nitrose to allow the use of a large excess of NO relative to NO_2 in the reaction chamber. As shown in Fig. 21, the solubility of N_2O_3 in sulfuric acid is much higher than the solubility of NO. This increased solubility occurs because an acid-soluble compound, nitrosylsulfuric acid, is formed which is obviously essential for efficient nitrogen oxide recovery.

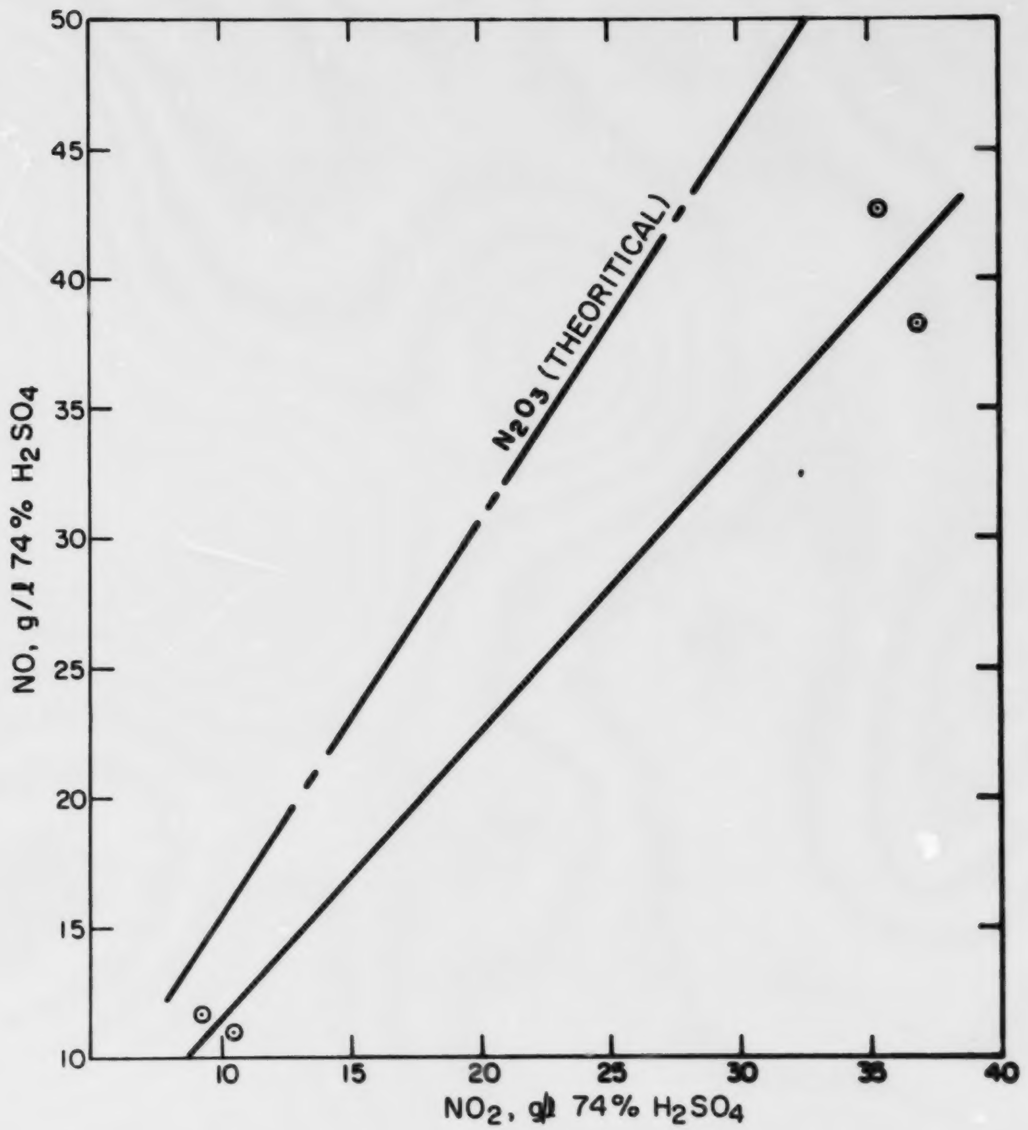


Fig. 20. Solubility of NO in 74% H_2SO_4 containing NO_2, 40°C.

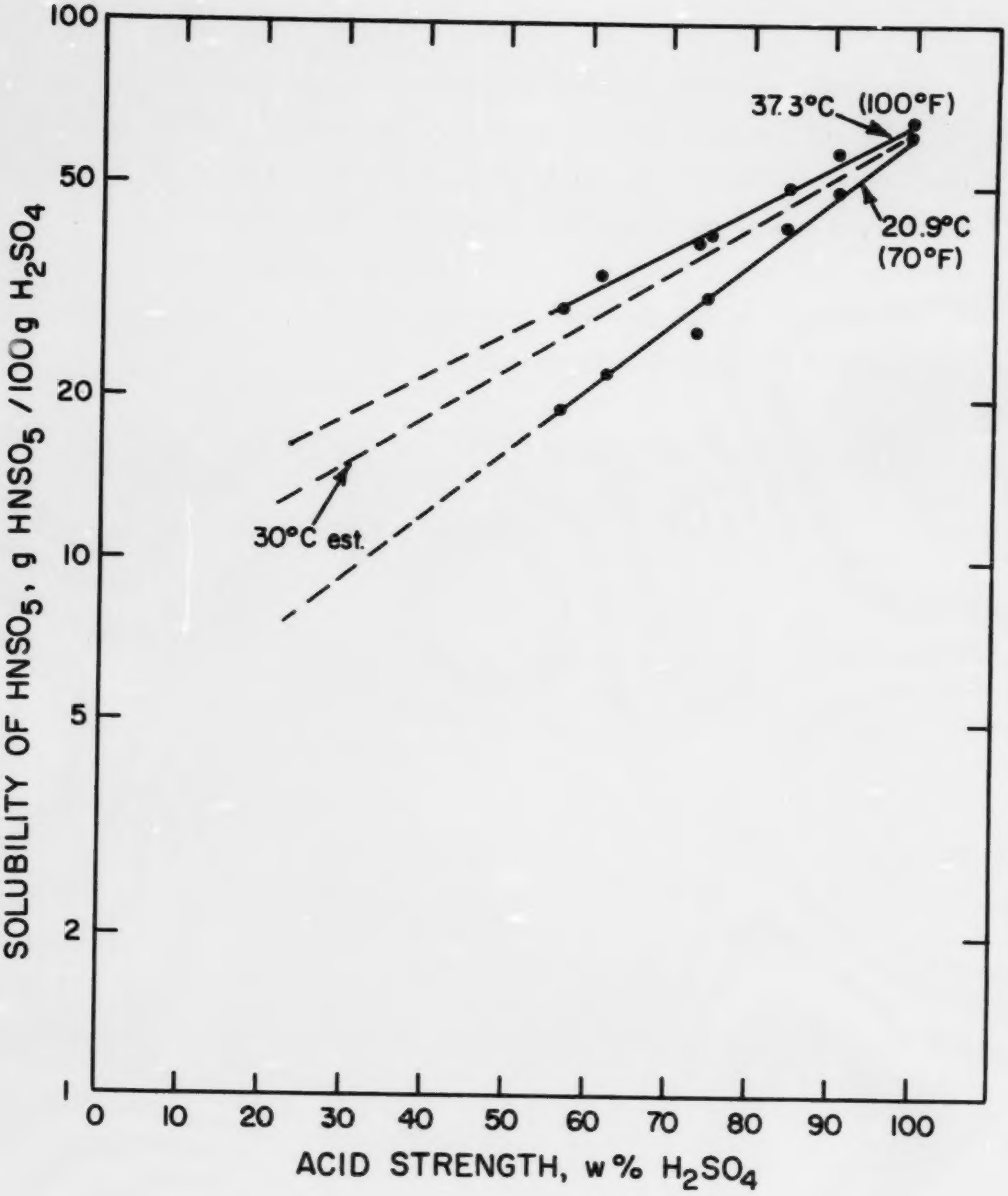


Fig. 21. Solubility of nitrosyl sulfuric acid in H_2SO_4(6)

Since this process envisions oxidation of SO_2 to sulfuric acid in the presence of fly ash, it was necessary to determine the extent of contamination of the sulfuric acid produced by contacting with fly ash. Samples of fly ash from a coal-burning power plant (New England Electric Co., Salem, Mass.) were obtained and contacted with sulfuric acid as shown in Table XI below. The amount of ash dissolved may be controlled by reducing the contact time before ash solids filtration.

TABLE XI Contamination of Sulfuric Acid by Fly Ash [*]

Contact Time Min.	Temp. °C	Acid Concentration % H_2SO_4	% of Ash Dissolved	Acid Analysis, % [†] Fe	Al	Si	Ca
120	25	30	4.95	.010	.018	.005	nil
30	25	30	5.97	---	---	---	---
120	25	70	8.86	.010	.023	.012	nil
30	25	70	7.51	---	---	---	---
120	75	30	20.6	.051	.015	.016	trace
30	75	30	9.3	---	---	---	---
120	75	70	16.1	.018	.008	.010	nil
30	75	70	10.2	---	---	---	---

---

[*] All experiments were performed using reagent grade sulfuric acid, with an initial ash concentration of 0.5% wt equivalent to that expected in an actual process.

[†] ASTM analytical methods used.

H. The Modified Chamber Process

1) Conceptual Change. The experimentation described in Sections D-G of Part V of this report indicates that the original Chamber Process concept for flue gas clean-up as presented in Section V-B cannot be used without modification. The primary drawback to the basic Lead Chamber Process is the difficulty in reoxidizing the NO formed during the SO_2 oxidation back to NO_2 for recovery and recycle. The long residence times required to reoxidize the very dilute NO would necessitate the use of impossibly enormous reaction chambers, making the process impractical.

As discussed in Section V-E, the way to avoid this extended reaction time is to collect the nitrogen oxides in sulfuric acid, concentrate them in a separate gas stream, and then oxidize the nitric oxide content before recycling the nitrogen dioxide to the reactor. This highly significant conceptual change makes it technically possible to use Chamber Process technology for removing sulfur dioxide from power plant flue gas and is incorporated in the process scheme shown in Fig. 22 and now called the Modified Chamber Process. Complete heat and material balances were necessary before an economic analysis could be made to determine if the modified process is economically feasible as well.

2) SO_2 Reaction Chamber. In the Modified Chamber Process the flue gas at 300°F is fed to the reactor chamber where it is mixed with nitrogen oxides so that the net mole ratio before SO_2 oxidation is $NO_2 : SO_2 : NO$ = 3:1:1. (See the total material balance, Table XII for details.) The purpose of using this mole ratio is to provide an excess of NO_2 in the reaction mixture to make sure that a maximum amount of sulfur dioxide is oxidized and still have an equimolar mixture of NO and NO_2 when the reacted gas enters the scrubber:

$$3\ NO_2 + 1\ NO + 1\ SO_2 \rightarrow 2\ NO_2 + 2\ NO + SO_3$$

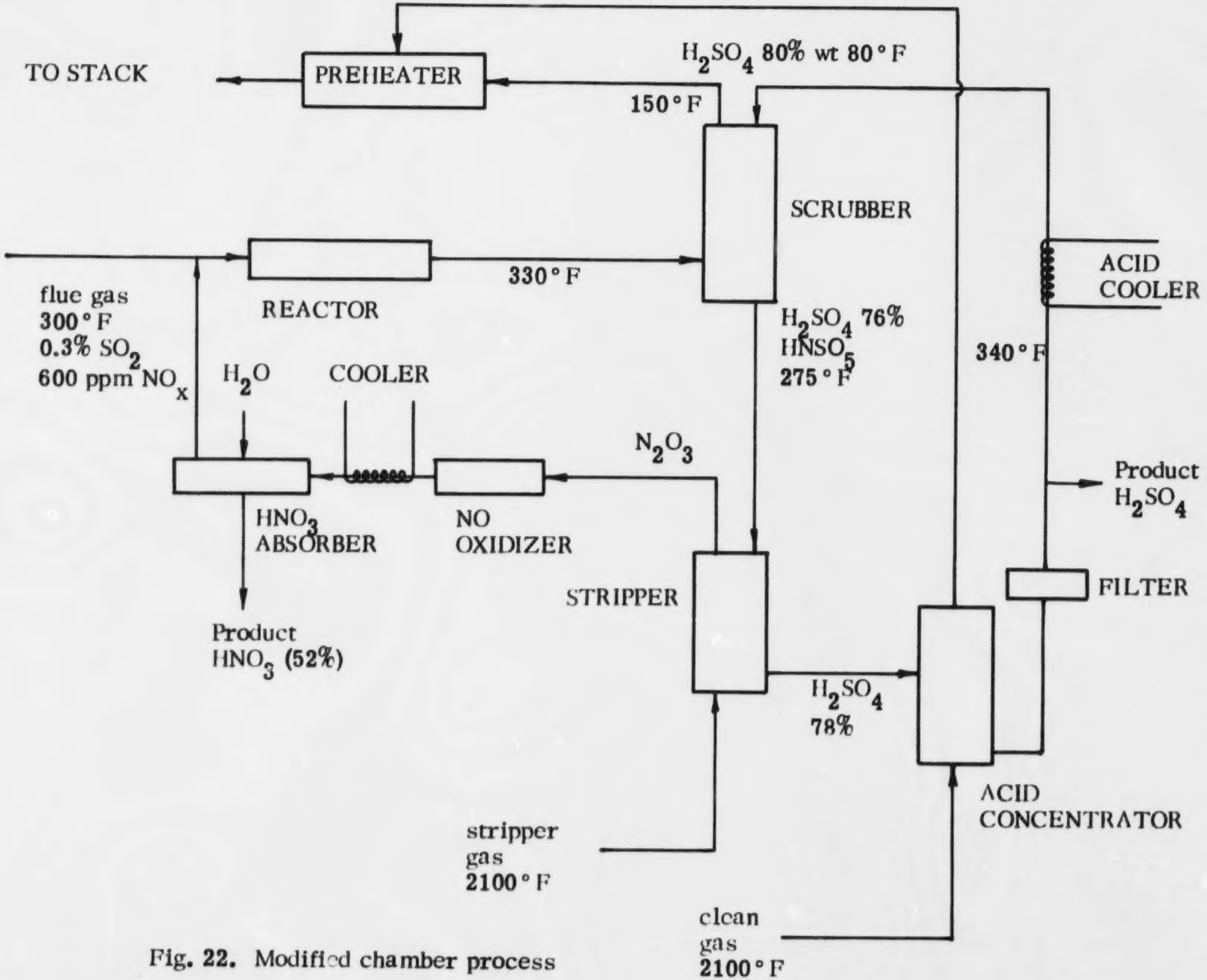

TO STACK
PREHEATER
H_2SO_4 80% wt 80 ° F
150 ° F
SCRUBBER
flue gas
300 ° F
0.3% SO_2
600 ppm NO_x
REACTOR
330 ° F
ACID
COOLER
H_2SO_4 76%
$HNSO_5$
275 ° F
340 ° F
H_2O
COOLER
N_2O_3
Product
H_2SO_4
HNO_3
ABSORBER
NO
OXIDIZER
STRIPPER
FILTER
Product
HNO_3 (52%)
H_2SO_4
78%
ACID
CONCENTRATOR
stripper
gas
2100 ° F
clean
gas
2100 ° F

Fig. 22. Modified chamber process

Table XII. Material Balance - Modified Chamber Process
(Basis: 1000 lb Flue Gas)

Stage	CO_2	H_2O	SO_2	O_2	N_2	H_2SO_4	Ash	NO_x	NO_2	NO	Total	T, °F
Flue gas to process	215	44	6.4	30	702	--	2.0	0.6	--	--	1000.0	300
Gas from cyclone	215	44	6.4	30	702	--	0.8	--	.03	.57	998.8	300
Gas from oxidizer	45.1	24.5	0	3.9	147	0	--	--	13.77	2.43	236.7	300
Gas from N_2O_3 mixer	260	66.7	0	32.3	349	9.8	0.8	--	9.20	6.00	1233.8	340
Recycle acid to collector (80% H_2SO_4)	---	300	--	--	---	1200	--	0	0	0	1500	80
Acid from collector (76% H_2SO_4)	---	362.6	--	--	---	1209.8	0.8	--	9.20	6.00	1588.4	285
Gas to stack	260	3.4	0	32.3	349	0	0	--	.003	.002	1144.7	150
Acid from stripper (78% H_2SO_4)	---	347.0	0	--	---	1211.8	1.2	0	0	0	1560.0	375
Gas to stripper	45.1	9.2	1.3	6.3	147	--	0.4	0.13	--	--	210	2100
Vapor from stripper	45.1	24.5	0	6.0	147	--	0	0	9.28	6.05	237.9	300
Acid from concentrator (80% H_2SO_4)	---	303	0	0	0	1211.6	0	0	0	0	1515	395
Fly ash cake	---	0.3	0	0	0	0.9	1.2	0	0	0	2.4	80
Product acid (80% H_2SO_4)		2.7	--	--	--	10.7	--	--	--	--	13.4	80
Gas to concentrator	39	8.0	0	5.4	128	--	0.4	0.1	--	--	181	2100
Exhaust from concentrator	39	52	0	5.4	128	--	0.4	0.1	--	--	225	400
Water to HNO_3 absorber	---	1.7	--	--	--	--	--	--	--	--	1.7	70
Vapor from HNO_3 absorber	45.1	24.5	0	6.0	147	0	0	0	7.7	6.4	222.6	300
Product HNO_3 (52%)	0	1.45	--	---	---	--	--	1.45 HNO_3	--	---	2.9	100
Water to acid cooler (no waste heat boiler)		2240									2240	70

The large heat of conversion of SO_2 to sulfuric acid does not result in a high temperature rise in the flue gas stream because the SO_2 concentration is at a low level. The reactor heat dissipation provisions necessary in the original chamber sulfuric acid process are unnecessary in this process, and the heat of reaction is removed by recirculated acid in the scrubber. The heat of reaction of SO_2 and dilution to 80% H_2SO_4 is about 1350 BTU/ lb 100% H_2SO_4. Formation of 9. 8 lbs. H_2SO_4/ 1000 lb. flue gas, for example, as shown in Table I, corresponds to a gas temperature rise of

$$\frac{9.8\ (1350)\ \text{BTU}}{0.241\ \frac{\text{BTU}}{\text{lb}^\circ\text{F}}\ \text{x}\ 1234\ \text{lb.}}\ ,\ \text{or}\ 44^\circ\text{F},$$

and part of this energy will be lost by radiation and convection to the surroundings. Also, since reoxidation of the NO formed in the reaction to NO_2 is performed externally to the main flue gas stream, higher temperatures in the flue gas do not adversely affect the rate, as they do in the conventional chamber process. (The rate of oxidation of NO to NO_2 decreases as the temperature is increased, while that of SO_2 to H_2SO_4 increases as the temperature is increased.)

3) Scrubber. In the packed bed scrubber the reacted gases are contacted with a countercurrent stream of cool, clean sulfuric acid which scrubs out the sulfuric acid mist formed in the reaction chamber along with the equimolar mixture of nitrogen oxides, the fly ash, and the water vapor in the gas. The clean, dry stack gas can now be vented to the atmosphere having been cooled to about 150°F. This will be heated for better dispersion as will be shown later.

Effective removal of both sulfuric acid and oxides of nitrogen from the gas stream is an essential part of this process. Vapor pressure data indicate that with an efficient gas scrubbing system, negligibly small amounts of H_2SO_4 or N_2O_3 will escape to the atmosphere. Both Berl[4] and Yushmanov [13] have measured the vapor pressure of N_2O_3 and water over sulfuric acid of various nitrose concentrations and temperatures. Fig. 23 and 24 illustrate these data for 80% wt H_2SO_4 solutions.

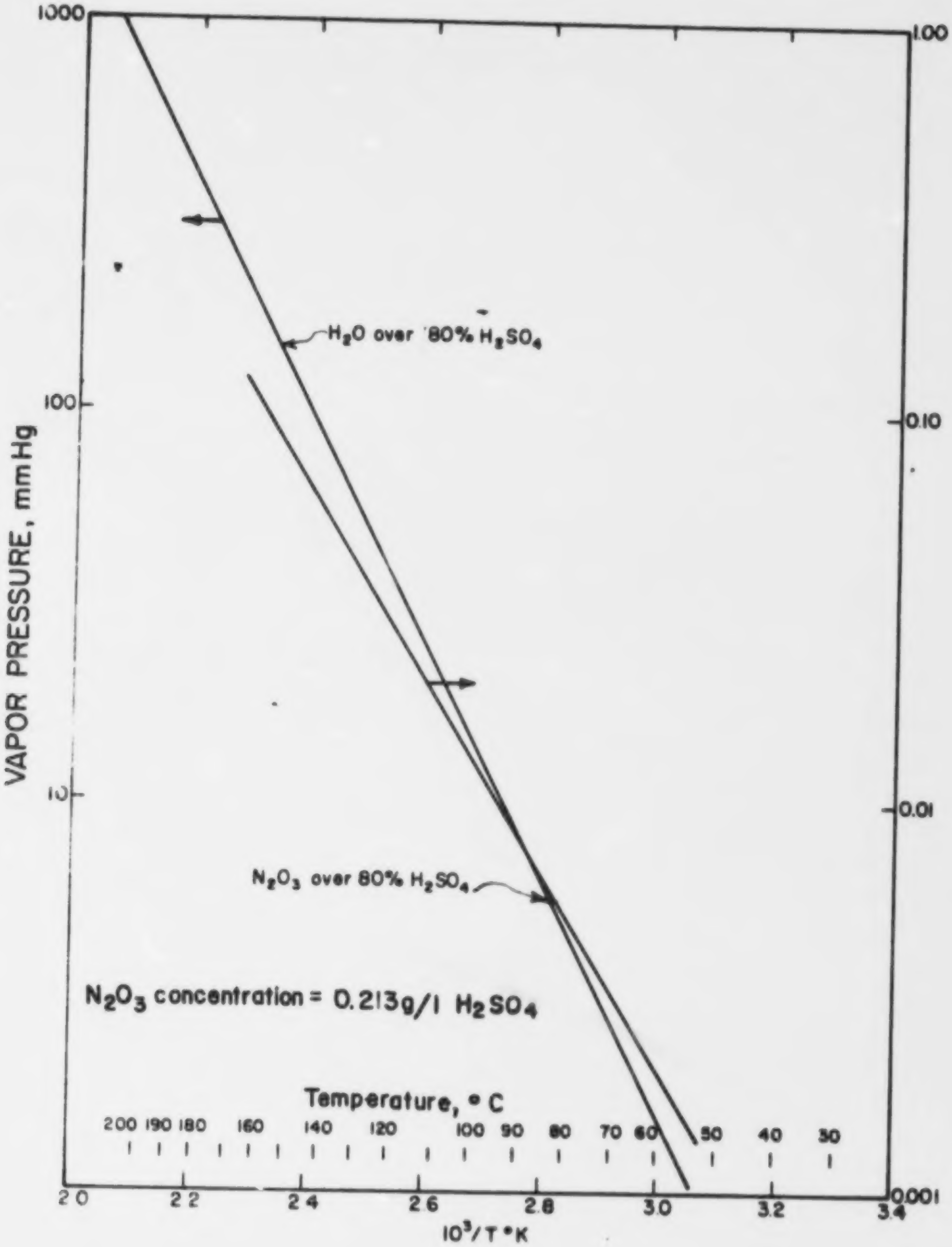


Fig. 23. Vapor pressure of N_2O_3 and H_2O over 80% H_2SO_4 solutions, Yushmanov.[13]

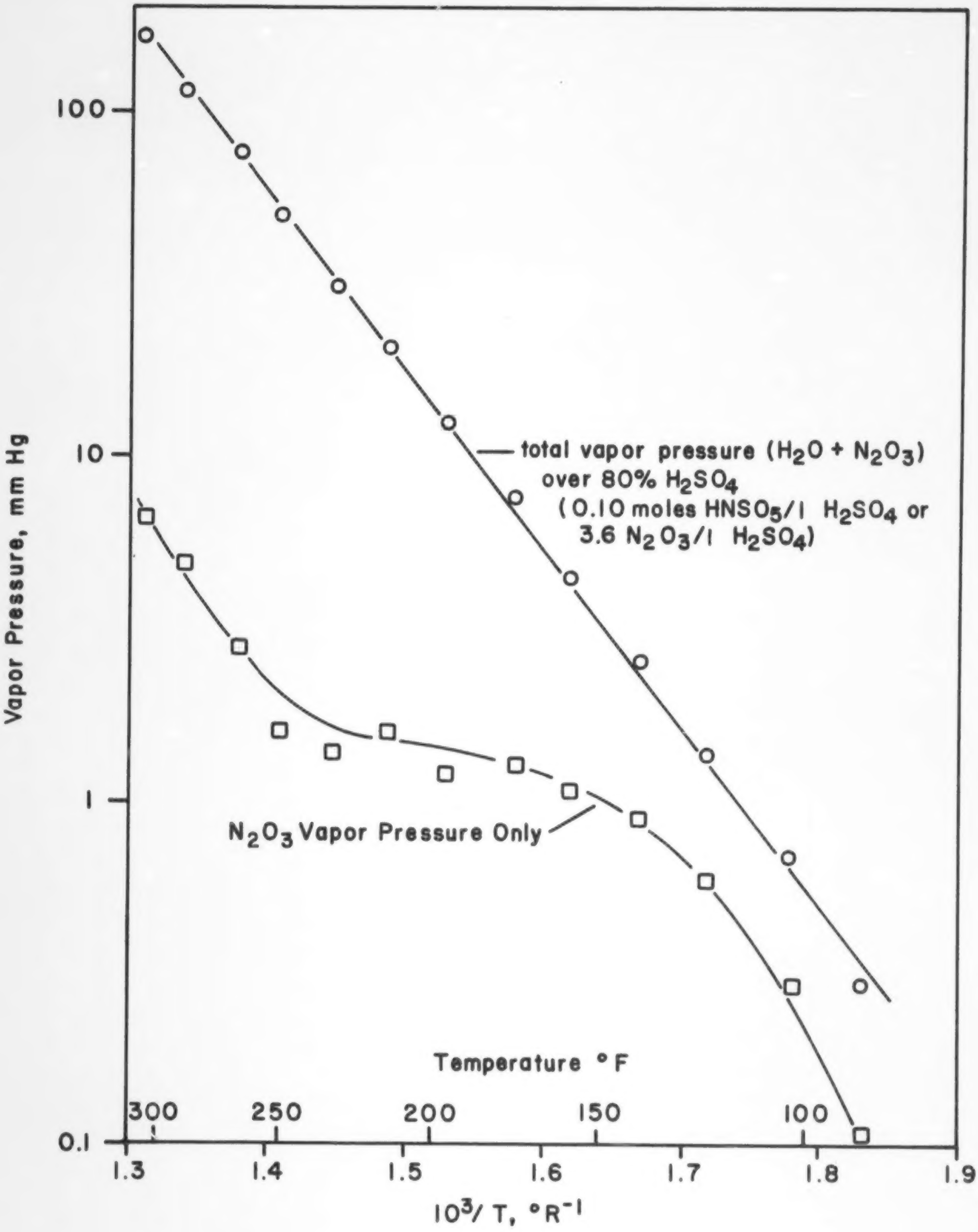


Fig. 24. Nitrose vapor pressures over 80% wt H_2SO_4 solutions (Berl and Saenger)[4]

After our experimental experience and an additional literature search, it was seen that the fiberglas packed mist eliminator would not be a practical NO_x scrubber because of the excessively high pressure drops through this kind of device. Laboratory experimentation with the small fiberglas packed absorber yielded pressure drops up to 36 inches of water, obviously too high to be useful. To overcome this resistance huge draft fans would be necessary in a 800 MW power plant handling almost 1.5 million cubic feet per minute of flue gas. There is clearly an advantage to minimizing the pressure drop through the scrubber. To attain lower resistance through this column it was decided to use more conventional packings: both rings and saddles offer lower pressure drop than the fiberglas packing. The primary advantage of the fiberglas, that of removing acid mists, is lost with conventional packings, but it is not clear at this stage of development how serious the mist problem will be. It was decided to go with standard ceramic packing and evaluate the mist problem at a later stage of development.

4) Nitrogen Oxide Recovery. The nitrose leaving the scrubber enters a packed bed stripper column where it is treated by a countercurrent stream of hot (2100 °F) flue gas. The nitrogen oxides are vaporized and pass out of the column with the carrier gas, having been concentrated by a factor of five compared to the original flue gas stream. This is sufficient to allow separate reoxidation in a reasonable volume before being recycled to the reaction chamber.

If this absorption and desorption of nitrogen oxides is performed efficiently enough, it is possible to reap a considerable economic benefit at this stage in the process. If the oxides are recovered at an efficiency of 96% or higher there will be a surplus of N_2O_3 above recycle needs because of the recovery of nitrogen oxides present in the raw flue gas. If part of this recycle stream is cooled and scrubbed with water, this surplus can be converted to marketable 52% nitric acid:

$$3\,NO_2 + H_2O \rightarrow 2\,HNO_3 + NO$$

The higher the nitrogen oxide content of the flue gas, the more nitric acid can be made and the greater the economic advantage.

5) Acid Concentrator. The acid which has been denitrated in the stripper is recycled to the scrubber, but first it must be concentrated to remove the water that was absorbed from the wet flue gas. This excess water is sufficient to dilute the acid from 80% in the incoming scrubber stream to 76% in the effluent. Some water is removed in the stripper during the vaporization of the nitrogen oxides, but it is still necessary to strengthen the acid from 78% back to 80%.

In the conventional Chamber Process the nitrogen oxide vaporization and the concentration are performed in the same stage: the Glover Tower. This can be done because the process is water deficient and the water that is stripped from the nitrose can be used in the chambers in the production of sulfuric acid. In the Modified Chamber Process for flue gas treatment, however, there is a large excess of water and if all the absorbed water is vaporized in the stripper and recycled to the reactor, there will be a steady buildup of water in the system. This is avoided by recycling only part of the water by vaporization in the stripper and to remove the remainder from the system completely in a separate acid concentrating step. Under steady state conditions, all the excess water that is absorbed by the H_2SO_4 is removed by boiling the stripper effluent in an acid concentrator.

The acid concentration step is accomplished by passing enough hot, clean (2100° F) flue gas countercurrent to the denitrated stripper acid to boil the acid and venting the wet gas to the atmosphere. This effluent gas stream is mixed with the stack gas from the scrubber tower, thus heating the scrubber gas sufficiently to provide adequate buoyancy for proper atmospheric dispersion. Since the gas is vented directly to the atmosphere, it must be clean enough not to be an air pollutant itself. This means that the source of the concentrator gas must be a furnace burning sulfur-free fuel, such as natural gas or desulfurized coal. The requirement for a "clean" fuel places an additional economic burden on the process, which will be evaluated in a later section.

6) Fly Ash Filtration. The concentrated acid is cooled from 395°F (the boiling point of 80% sulfuric acid) to 80°F and is recycled to the scrubber. If the system is scrubbing fly ash out of the flue gas, then the acid must be

filtered before recycling; the produce acid is removed from the stream after filtration. In order to avoid filtering the entire recycle acid stream, an alternative approach would be to allow the fly ash concentration in the acid to build up so that the ash removed with the product acid per unit time would be equal to the ash introduced with the flue gas in the same amount of time, and only the product acid need be filtered.

7) Heat Balance. Using the total material balance shown in Table XII, a complete heat balance can now be calculated for the Modified Chamber Process as described in this section. The heat balance on the same basis as the material balance is shown in Table XIII, while Table XIV presents the balance for an 800 megawatt power plant installation (1.44×10^6 SCFM of flue gas).

8) Economic Analysis. At this stage in the discussion it is now possible to perform a preliminary economic analysis for the Modified Chamber Process based on conceptual changes described in this section and the heat and material balances given in Tables XII, XIII, and XIV. The assumptions made in this analysis are listed in Table XV.

Table XVI shows a breakdown of the equipment type and size required for the Modified Chamber Process together with its estimated delivered cost. Using the same 3.29 factor as in Table IV, this data is then used to develop an estimate of the total capital cost as shown at the bottom of Table XVI. Based on the total capital cost and general guidelines for plant operation, the annual operating cost was developed in Table XVII. Taking credits of $20/ton (100% basis) for 80% sulfuric acid and $78/ton (100% basis) for 52% nitric acid, an income statement was calculated in Table XVIII showing a gross loss of $151,000 which corresponds to a loss $0.07/ton of coal. These figures show that the Modified Chamber Process will break even.

9) Overall Evaluation. The Modified Chamber Process appeared to to be economically feasible, but closer examination of the process revealed that there was some question as to the practicality of one significant operational aspect: the extra heat requirements in the stripper and the concentrator.

Table XIII. Heat Balance - Modified Chamber Process

Heat Inputs (Basis: 1000 lb. entering flue gas):

Cooling stack gas, 300 → 150°F: 1190 lb. x $\frac{0.241\ \text{BTU}}{\text{lb.}\ ^\circ\text{F}}$ x 150°F =	43,000 BTU
Cooling stripper gas, 2100 → 300°F: 224 lb. x .241 x 1800° =	97,200 BTU
Condensing water in recycle acid: (63 lb. - 15.3 lb.) x $\frac{1357\ \text{BTU}}{\text{lb.}}$ =	64,700 BTU
Heat of reaction, $SO_2 \rightarrow 80\%\ H_2SO_4$: 11.6 lb. H_2SO_4 x $\frac{1350\ \text{BTU}}{\text{lb.}}$ =	15,650 BTU
Cooling concentrator gas, 2100 → 400°F: 203 lb. x .241 x 1700° =	83,000 BTU
Total heat input per 1000 lb. flue gas =	303,650 BTU

Heat Outputs:

Cooling 80% H_2SO_4: 1515 lb. x $\frac{0.47\ \text{BTU}}{\text{lb.}\ ^\circ\text{F}}$ x (395° - 80°F) =	224,000 BTU
Water vaporized in concentrator: 44 lb. x $\frac{1357\ \text{BTU}}{\text{lb.}}$ =	59,000 BTU
Unaccounted for (6.6%) =	20,050 BTU
	303,650 BTU

Table XIV. Heat Balance: Modified Chamber Process for 800 Megawatt Power Plant Installation (7.25 MM lb/hr entering flue gas) (38.8 tons per hour 100% H_2SO_4 produced)

Input	Output
Cooling stack gas: 312 MM BTU/Hr	
Cooling stripper gas: 704 MM	Cooling water: 1717 MM
Condensing water in recycle acid: 469 MM	Water vaporized in concentrator: 484 MM
Cooling concentrator gas: 603 MM	
Total: 2201 MM BTU/Hr	2201 MM

Table XV. Assumptions for Economic Analysis

(1) 280 tons of coal burned an hour, flue gas composition as given in Table I.

(2) Flue gas rate 1.44×10^6 SCFM from an 800-megawatt power plant.

(3) Two percent of the sulfur in the coal burns to SO_3, the remainder to SO_2.

(4) Ash content of the flue gas 2 lb per 1000 lb.

(5) Yearly maintenance cost (labor, supervision, and material) equal to three percent of depreciation base.

(6) Plant facilities are charged at five percent of the cost of units, and plant utilities-seven percent of cost of units plus plant facilities.

(7) A total charge on investment of 14 percent annually is made to include taxes, insurance, and return on investment.

(8) SO_2 is quantitatively converted to H_2SO_4.

(9) Gas residence time in SO_2-oxidation chamber is two seconds.

(10) Gas residence time in reoxidation chamber is ten seconds.

(11) Recovered N_2O_3 from stripper contains 1 lb H_2O per lb N_2O_3.

(12) Pressure drop: twelve inches of water over entire system.

(13) SO_2 reactor temperature: 300° F.

(14) Sulfuric acid (80%) is sold for $16 per ton

(15) Scrubber efficiency for N_2O_3 and H_2SO_4:99.9%.

(16) Operating life of packing: two years.

Table XVI. Estimated Equipment Cost for Modified Chamber Process
(800 Megawatt Power Plant Installation)

Item	No. Required	Duty	Size	Estimated Purchase Cost, $
Cyclone separator	3	Remove coarse fly ash from flue gas	487, 000 cfm	245, 000
Re-oxidation chamber	1	Provide retention time for re-oxidation of NO to NO_2	183, 000 cfm, 10 sec. gas retention 30 ft. dia. x 43 ft. height	70, 000
Scrubber unit	3	Absorb N_2O_3, acid mist and ash	35 ft. dia x 70 ft. height. 8 ft. / sec gas velocity	1,500, 000
Stripping unit	2	Remove N_2O_3 for recycle from acid and water	32 ft. dia x 60 ft. height. 2 ft/ sec vapor velocity	250, 000
Coal furnace for stripper	1	Provide hot gas for stripper heat requirement	704 MM BTU/ hr	80, 000
HNO_3 absorber	1	Convert part of NO_2 to HNO_3 and remove as 52% HNO_3	44 ft. dia x 60 ft. height 183, 000 cfm 2 ft/ sec gas velocity	450, 000
Acid concentrator	3	Concentrate H_2SO_4 to 80% strength	360, 000 lb/ hr H_2O evap	300, 000

Table XVI(Cont.)

Item	No. Required	Duty	Size	Estimated Purchase Cost, $
Furnace for concentrator	3	Provide hot gas for concentrator	603 MM BTU/ hr	150, 000
Filter	3	11, 600 lb/hr cake	Rotary drum unit	250, 000
Acid cooler	3	Cool concentrated acid for recycle	Shell and tube exchangers, 21, 000 ft^2 area each, 400 MM BTU/ hr. each	320, 000
Product storage tank	3	Store cold 80% H_2SO_4	500, 000 gal. total volume	100, 000
Exhaust fan	3	Provide differential pressure for gas flows	12 in. water suction 87 MM SCFH total flow	60, 000
Total Equipment Cost (Purchased)				$3,855, 000
Total Capital Cost (Based on Factor of 3. 29 Developed in Table IV)			$12, 683, 000	

Table XVII. Annual Operating Cost Estimate: Modified Chamber Process (800 Megawatt Power Plant Installation)

Packing replacement	$ 75,000
Water, 23,600 GPM at $0.10/M gal	1,133,000
Direct labor	72,300
Supervision	10,800
Maintenance (0.05 of fixed capital)	634,200
Supplies at 15% of maintenance	95,000
Power, 24.2 MM Kw hrs at $0.006/Kwhr	145,000
Heat, 1307 MM BTU/hr at $0.50/MM BTU	5,220,000
Total direct cost	$7,385,400
Payroll burden (20% of direct labor and supervision)	16,600
Plant overhead (50% of direct labor and supervision, maintenance and supplies)	406,200
Packing and shipping	400,000
Waste disposal	25,000
Total indirect cost	$847,800
Depreciation (10% of fixed capital)*	$1,268,300
Taxes (2% of fixed capital)	253,700
Insurance (1% of fixed capital)	126,800
Total fixed cost	$1,648,800
Total Operating Cost	$9,882,000

* Assumes 10 yr straight-line depreciation.

Table XVIII. **Return on Investment:** Modified Chamber Process (800 Megawatt Power Plant Installation)

Credits	
80% Sulfuric Acid, 38.8 tons/hr (100%) at $20/ton	$ 6,201,000
52% Nitric Acid, 5.2 tons/hr (100%) at $84/ton	3,530,000
Total Credits	$ 9,731,000
Annual Operating Cost (Table XVI)	9,882,000
Gross Profit	(151,000)

Loss on investment before taxes $\frac{151,000}{12,683,000} = 1\%$

Cost \$/ton coal $\frac{151,000}{280 \times 8000} = \$0.07$

Calculations show that these two stages require about 37% more heat than the power plant generates, implying that an additional 37% more coal would have to be burned, about half of which must be sulfur-free. It is true that the economic analysis showed that this could be done and still break even, but it was felt that there would be considerable resistance in the power industry to putting in enough furnace capacity to consume 37% more fuel than was currently being burned. Efforts would have to be made to further modify the process to limit the extra heat requirements.

It was therefore decided to continue work on the experimental verification of the Modified Chamber Process while concurrently working on new schemes to reduce heat requirements. The remainder of this section of the report will discuss in turn: 1) the laboratory work aimed at establishing the feasibility of the Modified Chamber Process and 2) the conceptual and laboratory work intended to reduce the heat requirements of the process thereby improving both the economics and commercial practicability.

I. Laboratory Evaluation of the Modified Chamber Process

Initially it was decided to divide the laboratory feasibility studies for the evaluation of the Modified Chamber Process into two phases: a 1 SCFM bench scale evaluation of individual process stages, and a 10 SCFM pilot plant analysis of an integrated system. Initial work with a bench scale scrubber system demonstrated that this scale of study would not be practical because the efforts necessary to optimize the individual process stages would take far more time than they merited and would unreasonably delay the scale-up to the pilot plant. It was felt that the optimization of the individual stages of the process could be accomplished just as rapidly and far more meaningfully in the pilot plant stage than on a bench scale.

The bench scale scrubber experiments did have appreciable value although they were not carried through to complete optimization. Using a 3 foot column, 2 inches in diameter, packed with 1/4 inch Berl saddles, absorption studies were carried out by countercurrent scrubbing of an artificial flue gas (NO_2:NO:SO_2::3:1:1 in a nitrogen carrier gas) with 80%, 80 °F sulfuric acid at an L/G ratio of 1.03. Absorption efficiencies of about 90% for both SO_2 and NO_2 were determined by ultraviolet spectrophotometric analysis of the effluent gas stream although maximum absorption was not obtained for both gases at the same time. Typical data for these experiments are shown in Figure 25 with the packed column described above being used as a scrubber. The NO and NO_2 flow rates were held constant at a 3:1 ratio while the SO_2 constant of the gas mixture was varied from a NO_2/SO_2 ratio of about 3.0 to 1.5.

The data in Figure 25 show high SO_2 removal efficiencies at high NO_2 excesses, while the NO_2 removal goes toward a maximum at low NO_2 excesses. This suggests that the NO_2 oxidation of SO_2 is not going to completion in the reactor and for the most part the NO_2/NO ratio is not near enough to equality to allow complete absorption in the scrubber.

These experiments, which show the difficulty in obtaining NO_2 removal efficiencies approaching 100%, have prompted a closer look into the mechanism of the adsorption of NO and NO_2 into sulfuric acid. An extensive literature search has resulted in the compilation of a large amount of information on the physical and chemical properties of nitrosyl sulfuric acid, but more data was needed in order to determine what was occurring in our system.

The experiment was set up such that a mixture of NO and NO_2 in nitrogen was passed through the reaction chamber and into the scrubber, with the scrubber effluent gas being monitored for NO_2 by means of the UV spectrophotometer. The two conditions that were varied were the ratio of NO to NO_2 and the gas flow rate. The sulfuric acid flow rate was held constant, as was the NO_2 concentration in the nitrogen carrier gas (0.9%). Figure 26 shows the NO_2 removal efficiency as a function of NO/NO_2 ratio at different contact times.

Two features of the data are obvious: that NO_2 removal efficiency increases with both NO/NO_2 ratio and with contact time.

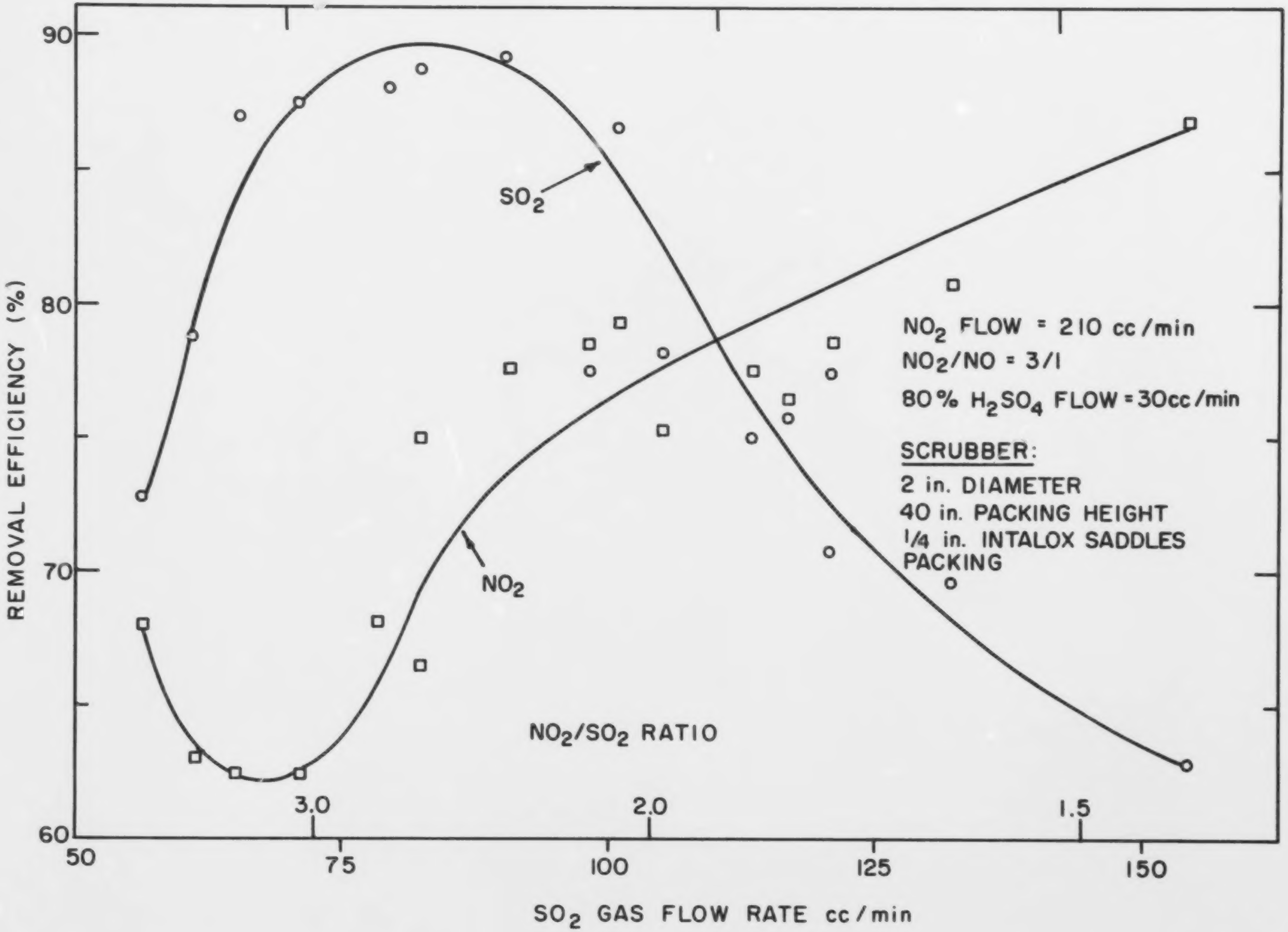


Fig. 25. SO$_2$ and NO$_2$ recovery efficiency in a packed bed scrubber

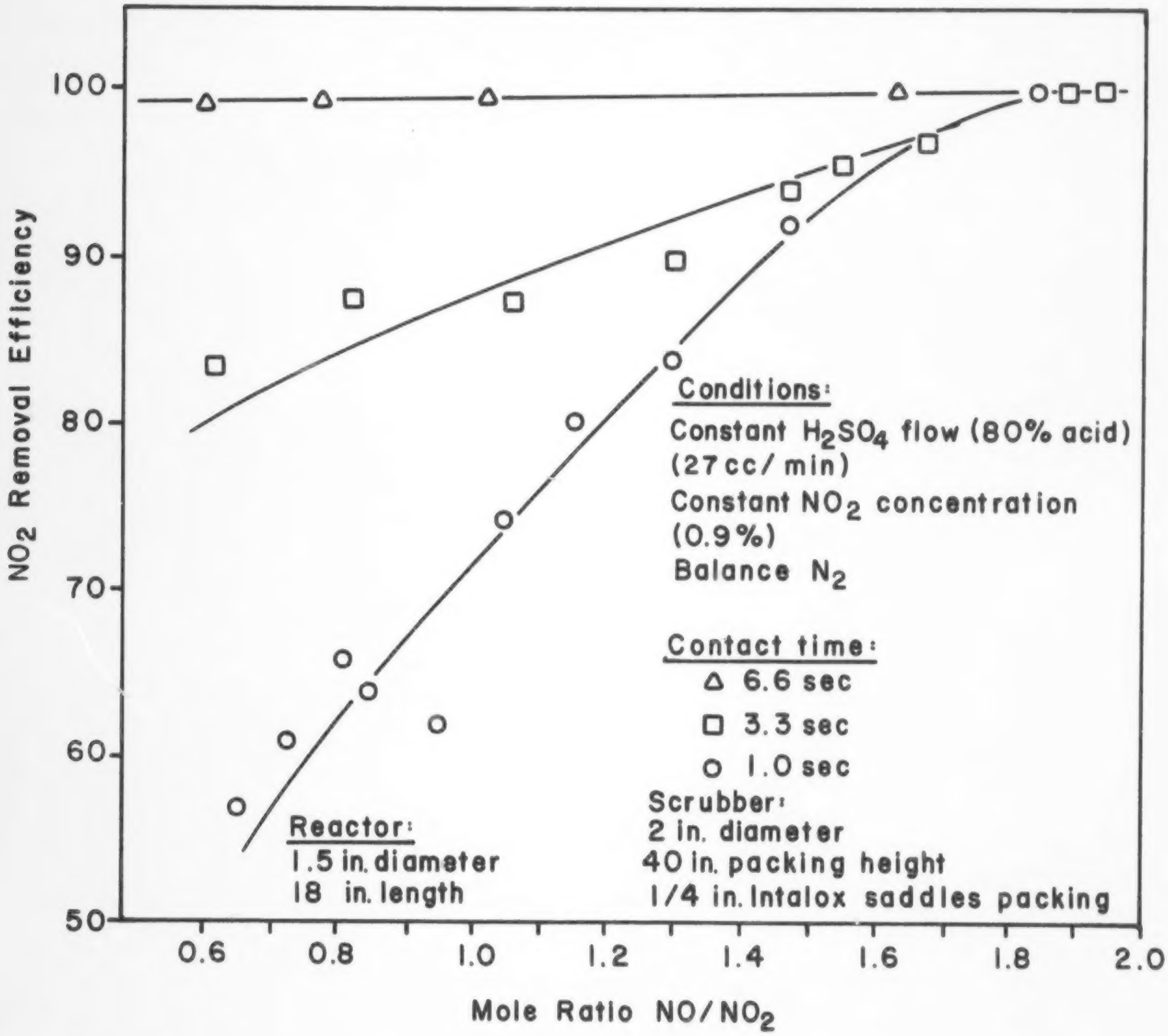


Fig. 26. NO_2 removal efficiency as a function of NO concentration and contact time

The fact that the NO_2 removal efficiency improves with increasing NO content (in the lower two curves) indicates that NO_2 is being removed as $HNSO_5$ (nitrosylsulfuric acid), at least in part. The fact that the gas is not completely removed at an NO/NO_2 ratio of 1.0 (the stoichiometric ratio for $HNSO_5$ formation) suggests that the absorption reaction did not go to completion, either because the gas-liquid contact time was insufficient for complete reaction, or the equilibrium at the timperature used did not allow it.

The increase in NO_2 removal with increased gas-liquid contact time may be due to two effects: additional formation of $HNSO_5$ or dissolution of NO_2 in sulfuric acid. The fact that 100% of the NO_2 was removed at NO/NO_2 ratios below 1.0 (top curve of Fig. 26) suggests that NO_2 is soluble enough to be absorbed alone in sulfuric acid. Experimentation has shown that 25 - 55 % removal of NO_2 at 0.0 NO/NO_2 can be achieved with the bench-scale scrubber, with the exact level being dependent on gas-liquid contact time. Comparison of this data with published literature shows agreement and points out the possibility of removing all oxides of nitrogen as long as the NO/NO_2 ratio is maintained at $\leq$ 1.0.

The work described above was very useful in determining operating information which could be of value in pilot plant operation: It established the importance of controlling the NO/NO_2 ratio of the reacted gas stream entering the scrubber, and showed that consideration must be given to such matters as accurate flow meter calibration, gas and liquid stream temperature control, and accurate, complete analysis of all streams to permit the calculation of material balances, and thus verify absorption efficiencies. These matters were kept in mind during the design and construction of the 10 SCFM pilot plant which is discussed in the next section.

J. The 10 SCFM Pilot Plant: Design, Construction, and Operation

1) Choosing a Basic Process Construction Approach. Three alternative schemes were considered for pilot plant construction: Pfaudler's "Glassed Steel" equipment, Corning's "Glassplant" system, or a beefed-up laboratory type system such as might be available from any of several laboratory supply houses. The features that were considered in evaluating each of these systems included durability (the ability of the completed system to withstand a wide variety of possible operating conditions and some physical punishment while being run on a round-the clock basis), versatility (the capability for easy change of components) and cost.

The Pfaudler "Glassed Steel" system utilizes steel equipment that is internally protected from corrosive process materials with a layer of fusion-bonded glass. It is quite rugged and is widely used in full scale plants that handle corrosive materials or food products. It can be obtained in a wide variety of individual components, which would allow considerable versatility, but, as would be expected, it is the most costly of the three systems. One other disadvantage of the Pfaudler system was the fact that we would be working at the very bottom of their size range, which might make it difficult to obtain certain components.

The Corning "Glassplant" system utilizes heavy duty glass components for use in small plants in the food and corrosive product industries. The system is surprisingly rugged, and they manufacture some rather large process units (including such items as 40 foot absorption towers and 50 gallon reactors). The equipment was available in "kit-form" and is very versatile with the cost being lower than the Pfaudler system. Again we would have been working at the low end of the size range, but it appeared that a complete range of components was available in the size desired.

The laboratory type equipment available from custom suppliers such as Ace Glass and Scientific Glass could have been designed and built to meet our specifications, but here we would have been working at the very top of their size range. Components such as columns for the absorber and stripper would have had to have been custom blown to our design and would have lacked a good deal in ruggedness and versatility. The cost was undoubtedly the lowest of the three systems, but not as low as expected.

Based on this overall system analysis the decision was made to use the Corning Glassplant Flanged Conical Pipe System in fabricating major components as well as for the connecting piping. Although somewhat higher in cost than the custom glass blown system, the advantages of using interchangeable stock items of industrial quality more than compensated for the increased cost.

Figure 27 presents a schematic diagram of the pilot plant system with Table XIX giving the cost of the various pieces of equipment. The design considerations for each stage will be discussed separately below.

2) Flue Gas Supply. In supplying a flue gas to the system, there are two obvious alternatives: using a coal burner to make "real" flue gas, or putting together an artificial flue gas from pure gases. Upon close examination it became clear that it would be far too expensive to obtain a

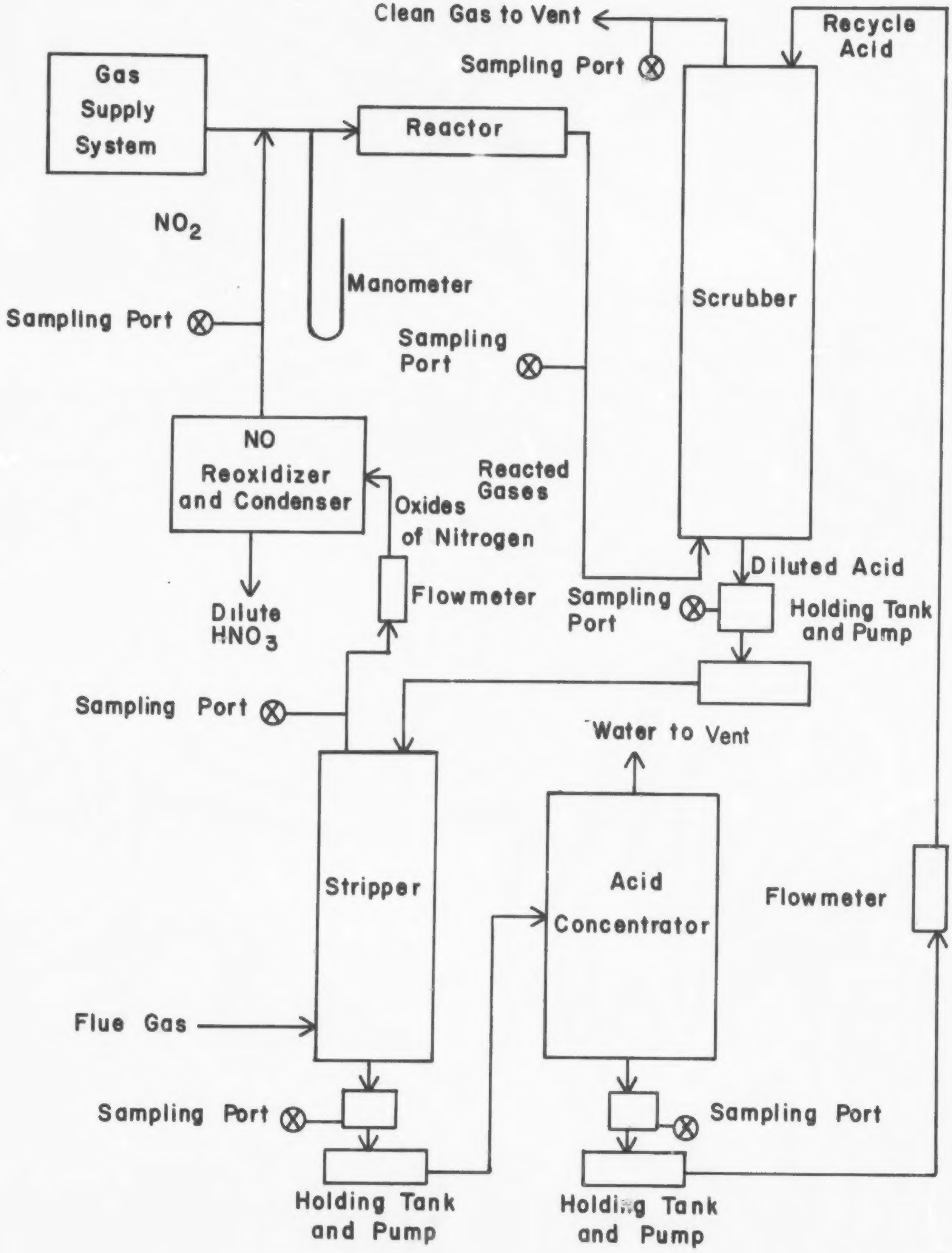

Clean Gas to Vent
Sampling Port
Recycle Acid
Gas Supply System
Reactor
NO2
Manometer
Sampling Port
Scrubber
Sampling Port
NO Reoxidizer and Condenser
Reacted Gases
Oxides of Nitrogen
Dilute HNO3
Flowmeter
Sampling Port
Diluted Acid
Holding Tank and Pump
Sampling Port
Water to Vent
Stripper
Acid Concentrator
Flowmeter
Flue Gas
Sampling Port
Sampling Port
Holding Tank and Pump
Holding Tank and Pump

Fig. 27. Flow sheet for 10 SCFM pilot plant

Table XIX. Cost of 10 SCFM Pilot Plant

1.	Flue gas supply system	$ 1100
2.	Reactor gas supply	880
3.	Reactor	370
4.	Scrubber	1460
5.	Stripper	1100
6.	Acid concentrator	960
7.	NO oxidizer	475
8.	Heating jackets	700
9.	Sulfuric acid pumping system	1000
10.	Piping and fitting	900
11.	Sampling port assemblies	1100
12.	Packing (3/ 8" Intalox Saddles)	250
		$ 10, 295

coal burner (about $10,000), aside from the fact that small coal burners do not really supply a flue gas representative of a power plant.

An artificial flue gas can be made up to any composition desired by mixing pure gases. The advantages are fairly obvious: the gas composition can be made to order, thus excluding oxygen if desired, and the capital outlay is relatively small. The disadvantages include high gas cost, a dependence on suppliers to maintain fairly high volumes of gas, and the fact that the gas would be quite different from real flue gas.

An alternative compromise scheme would utilize a natural gas burner to provide a stream of hot moist flue gas which would approximate the flue gas from a coal burning power plant if it were doped with sulfur dioxide and fly ash. The gas would be too hot to use directly, but it might be possible to use the vent gas from a commercial hot water heater where the gas temperature would be relatively close to the 300 ° F needed for the experimentation.

Further analysis of this last flue gas supply system (the natural gas burner) shows that the raw flue gas from a natural gas burner must be diluted because of its high water content but still offers the superior system. The natural gas, which is 95% methane, produces combustion gases which contain about 16% water, as compared to the combustion gas of a coal burner which contains about 5 - 7% water. If the flue gas from natural gas were to be used, the water concentration would have to be reduced, either by removing some of the water (which is impractical at elevated temperatures) or by diluting the flue gas.

The flue gas from a standard natural gas burner is produced at about 1400 ° F with 16% water. If the water content were to be diluted back to 5% it would mean mixing the flue gas with 70 ° F air at a 2/1 ratio. The resulting gas would be at a temperature of about 500 ° F, within the desired range. This diluted gas would have an oxygen concentration of 15% which could have some effect on the concentration of NO produced during the oxidation of SO_2 by the NO_2. Although the oxygen would be present in large excess of the stoichiometric amount needed to reoxidize the NO back to NO_2, the low concentration of NO in the flue gas and the short contact time of the mixture before it reaches the scrubber would probably prevent NO from being oxidized.

According to Burdick,[11] it would take 15 minutes for a gas containing 2% NO and 3% O_2 to attain 90% reaction at 77°F. The system currently under consideration would contain about 0.3% NO and 15% O_2. Considering that the reaction rate is directly proportional to the square of the NO concentration and to the first power of the oxygen concentration, it would take about 135 minutes to attain the same degree of reaction in the new system at the same temperature. Since the reaction rate decreases with temperature increase, very little NO will react during the few seconds it is in contact with oxygen at 300°F before it enters the scrubber.

Thus it appears that a diluted combustion gas from a natural gas burner would give us a flue gas of the proper water composition in the desired temperature range. The equipment needed would simply be a small gas burner, rated at 0.25 cfm of natural gas to deliver 10 cfm of hot flue gas. Natural gas is mixed with combustion air at a ratio of 10/1, giving about 2.75 SCFM of 1400°F flue gas which is then diluted 3/1 with room temperature air to give 11.0 SCFM at 400°F. This product can then be run through a simple heat exchanger to drop the temperature to any desired level. The same heat exchanger can be used to raise the temperature if any future testing requires hotter gases. (Hotter gases can also be obtained by lower dilution ratios, but this would of course change the water content of the product.)

Based on this analysis, the natural gas burner system was selected for the pilot plant. Any disadvantage in gas handling was more than offset by a distinct advantage in operating cost. An artificial flue gas system using nitrogen from a cryogenic supply system as the carrier gas would have cost about $400 per month to operate while the monthly natural gas cost is essentially negligible. (See Table XX for cost analysis.)

3) Reactor Gases. During the bench scale experimentation, oxides of nitrogen were supplied individually from cylinders of pure gases. This has worked out quite well for all gases except NO_2 which is a liquid at room temperature.

Table XX. Comparison of Alternative Flue Gas Supply Systems

	Natural Gas Burner		Liquid Nitrogen System (Reactant Gases Added)	
Flue Gas Composition (% by volume)	O_2	15.6	O_2	0.0*
	N_2	77.1	N_2	94.7
	CO_2	2.0	CO_2	0.0*
	H_2O	5.0	H_2O	5.0
	SO_2	0.3	SO_2	0.3
		100.0		100.3
Capital Equipment Costs	Gas Burner	$100	Heat Exchanger	$300
	Fan	75		
	Heat Exchanger	200		
		$375		$300
Monthly Operating Costs†	Natural gas	$ 2.50	Nitrogen	$450
			Equipment Rental	40
				$490
Total Annual Operating Cost and Equipment cost	$405			$ 6180

* Can be added if desired.

† Based on a 22 - day month and a 5 - hour day.

The flow of liquid NO_2 from the cylinder is therefore difficult to meter and control. It was therefore decided to supply NO_2 by mixing NO with air and providing enough residence time in a small reactor to allow complete oxidation to NO_2 in a relatively dilute form. As long as the partial pressure of NO_2 is below 0.75 atmospheres it will not condense at room temperature and will be easy to handle. SO_2 will be fed to the system directly from a cylinder as shown in the complete gas system schematic in Fig. 28. As discussed in the previous section, water will be supplied by the combustion gas from the gas burner and the H_2O concentration will be measured by a hygrometer in a small bypass stream.

4) Reactor. Continuous gas phase reactions are usually carried out in pipe-like reactors, with the volume of the pipe depending on the residence time necessary for complete reaction. Studies performed earlier have shown that 1.5 seconds is sufficient for complete oxidation of SO_2 under the conditions existing in the proposed system. With a flow of 10 SCFM and a reactor temperature of 300°F, the reactor volume would have to be 0.40 ft^3. Figure 29 shows the pipe-type reactor designed around the Corning Conical Pipe System which will allow changes in reactor volume by addition of lengths of standard 4" pipe.

Provisions will be made to insulate the reactor to simulate actual process conditions, although some heat loss can be tolerated. As is shown in the diagram, the temperature will be monitored at several points in the system. The pressure drop in the gas line (i.e., through the reactor and the scrubber) will be measured by a manometer placed on the upstream side of the reactor. From preliminary studies, it was anticipated that most of the pressure drop will occur through the scrubber since that is the only place where there is an obstruction in the line (packing).

The reactive gases (NO, SO_2, NO_2) will be introduced into the line just before the reactor. No insulation is to be used on the piping since the 1" glass pipe (5/32" wall thickness) should not lose much heat at the high gas velocities being used.

5) Scrubber. The scrubber is to be a countercurrent gas absorption column packed with glass Raschig rings. The column will be constructed of Corning glass sections to allow us to vary the packing height from 1 - 10 ft.

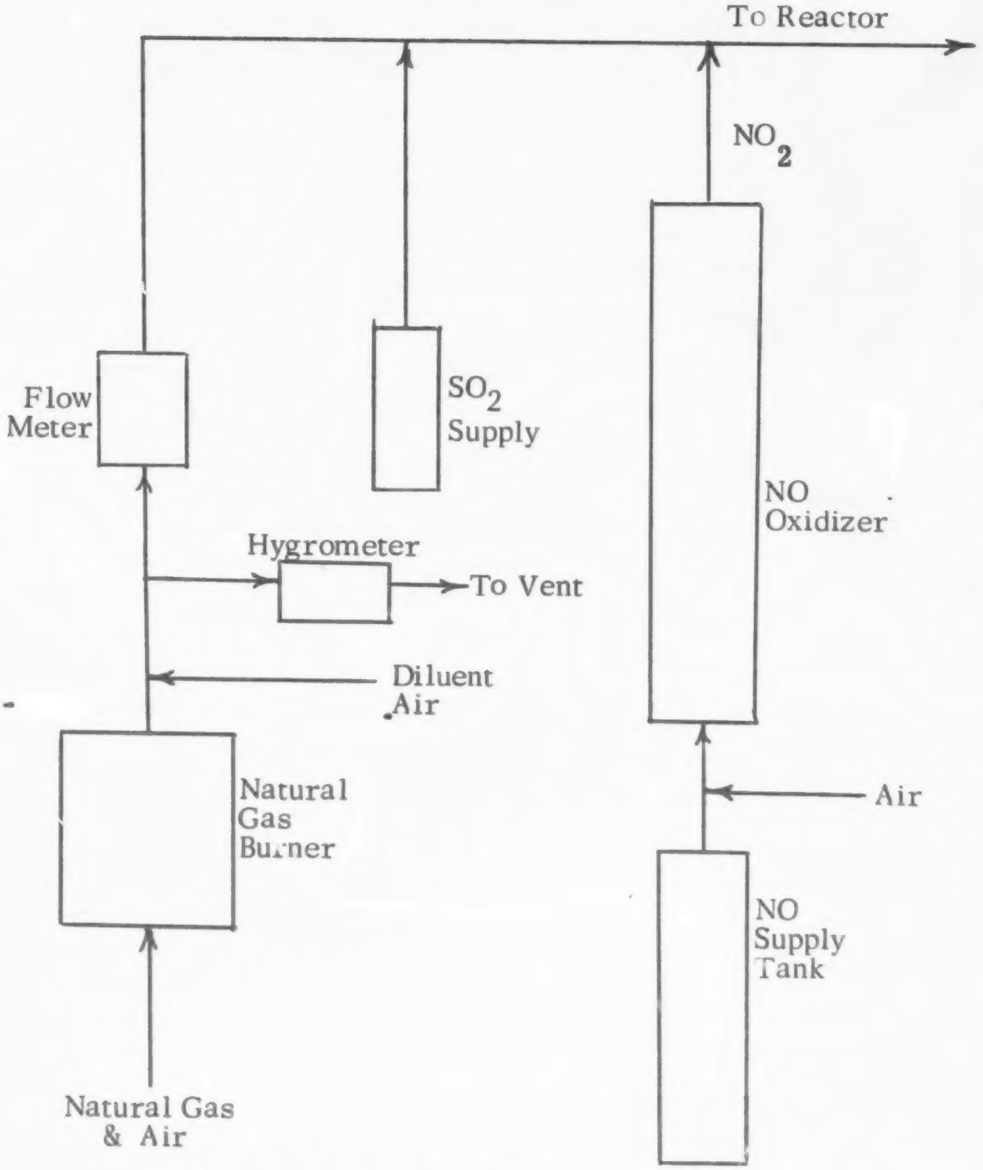

To Reactor
NO$_2$
Flow Meter
SO_2 Supply
NO Oxidizer
Hygrometer
To Vent
Diluent Air
Air
Natural Gas Burner
NO Supply Tank
Natural Gas & Air

Fig. 28. Gas Supply System - Pilot Plant

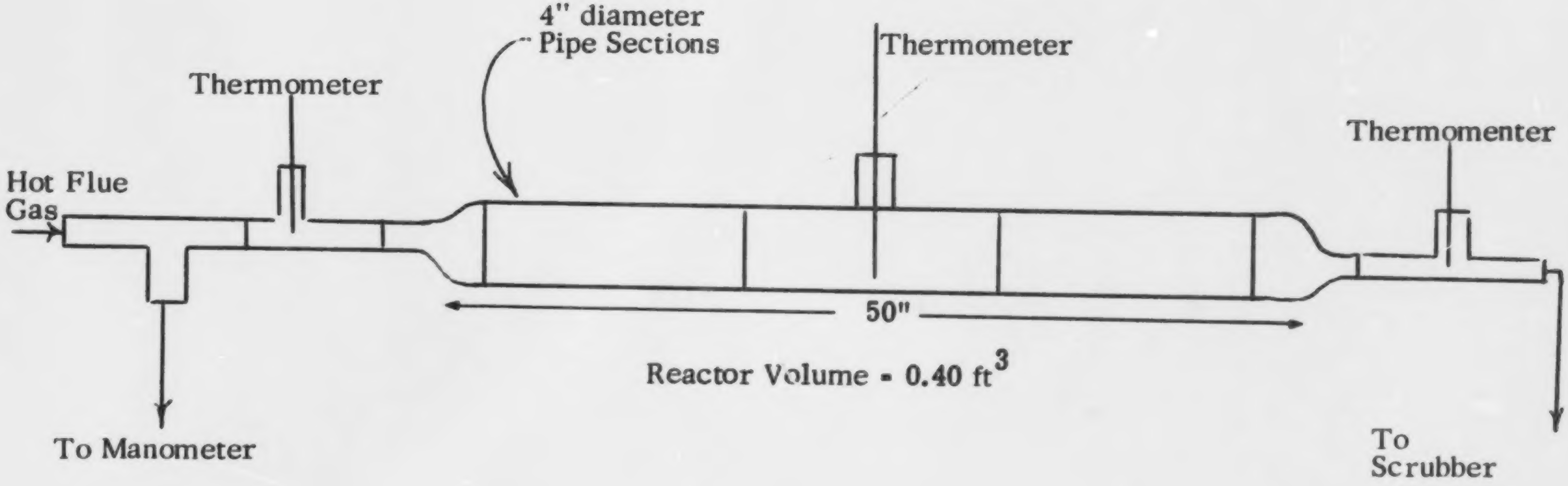

4" diameter
Pipe Sections
Thermometer
Thermometer
Thermomenter
Hot Flue
Gas
To Manometer
50"
Reactor Volume = 0.40 ft^3
To
Scrubber

Fig. 29. Pilot Plant Reactor

The absorber column diameter required for 10 SCFM of flue gas was calculated using the empirical method described by McCabe and Smith.[14] The general approach is to determine the gas flooding velocity of the column containing a certain packing and pick a column diameter which will result in an optimum gas velocity equal to one-half the flooding velocity. (Justification for the optimum choice of one-half the flooding velocity can be found in Sherwood and Pigford,[15] "Absorption and Extraction ").

A logarithmic plot of the group $G_y^2 a_v (\mu_x')^{0.2} / g_c \epsilon^3 \rho_x \rho_y$ versus the group $(G_x/G_y)\sqrt{\rho_y/\rho_x}$ was determined empirically for a great many systems. The parameters are:

G_x = mass velocity of liquid, lb/ ft^2-hr
G_y = mass velocity of gas at flooding, lb/ ft^2-hr
ρ_x = density of liquid, lb/ ft^3
ρ_y = density of gas, lb/ ft^3
a_v = surface area of dry packing per unit packed volume, ft^2/ft^3
μ_x' = viscosity of liquid, cp
g_c = Newton's law conversion factor, 4.17×10^8 ft/ lb/ lb force-hr^2
ϵ = porosity, or fraction voids, in packed section

In our system the gas flow rate is set at 10 ft^3/ min and G_xG_y calculated to be 1.5. The values of the other parameters are given below:

ρ_x = 1.64 lb/ ft^3 at 225° F
ρ_y = 0.0582 lb/ ft^3 at 225°F
a_v = 122 ft^2/ft^3 } for 1/2" Raschig rings
ϵ = 0.64 }
μ_x' = 1.4 cps (77% sulfuric acid at 250° F)

Some of these values are averages or approximations, but the errors introduced are considered to be small, probably under 10%, and it turns out that the value of G_y is relatively insensitive to even larger variations in these parameters.

The value of the group $G_x/G_y\sqrt{\rho_y/\rho_x}$ was calculated and for the chosen conditions is 0.0357. Using the empirical curve from McCabe and Smith (Fig. 30) the value of the group $G_y^2 a_v (\mu_x')^{0.2}/g_c \epsilon^3 \rho_x \rho_y$ was determined to be 0.17. Solving for G_y gives a gas flooding velocity of 920 lb/ft^2 hr. The mass gas flow is

$$10 \text{ ft}^3/\text{min} \times 60 \text{ min/hr} \times 0.0582 \text{ lb/ft}^3 = 34.9 \text{ lb/hr}$$

Assuming an optimum gas velocity of one-half the flooding velocity, the cross-sectional area of the column is

$$\frac{34.9 \text{ lb/hr}}{920/2 \text{ lb/ft}^2\text{-hr}} = 0.0758 \text{ ft}^2$$

This is the cross-sectional area of a column with a diameter of 3.75 inches. As a result, the column diameter was chosen to be 4 inches.

Since proposed process modification calculations have shown that it might be possible to run the scrubber at considerably lower liquid to gas ratios, the optimum column diameter calculation was made again. Based on the revised calculations discussed in an earlier report, a value of 0.45 was used for the parameter G_x/G_y instead of 1.5. The optimum column diameter for this new system was calculated to be 3.58 inches. Obviously the 4 inch column will be appropriate for a wide variety of conditions as long as the gas flow rate is kept at 10 SCFM.

An effort was made to calculate the optimum height of the column, but the mass transfer coefficients necessary to obtain reasonably accurate values are not available. Therefore, a variable height column was designed.

Figure 31 shows the schematic diagram for the design of the scrubber using the Corning system. This column sections are 1 foot long, making the apparatus quite versatile. The feed sections in the column are for the purpose of introducing the gas feed stream at different heights without completely disassembling the tower. These sections will also be packed and are provided with thermometer ports for monitoring the column temperature at different points.

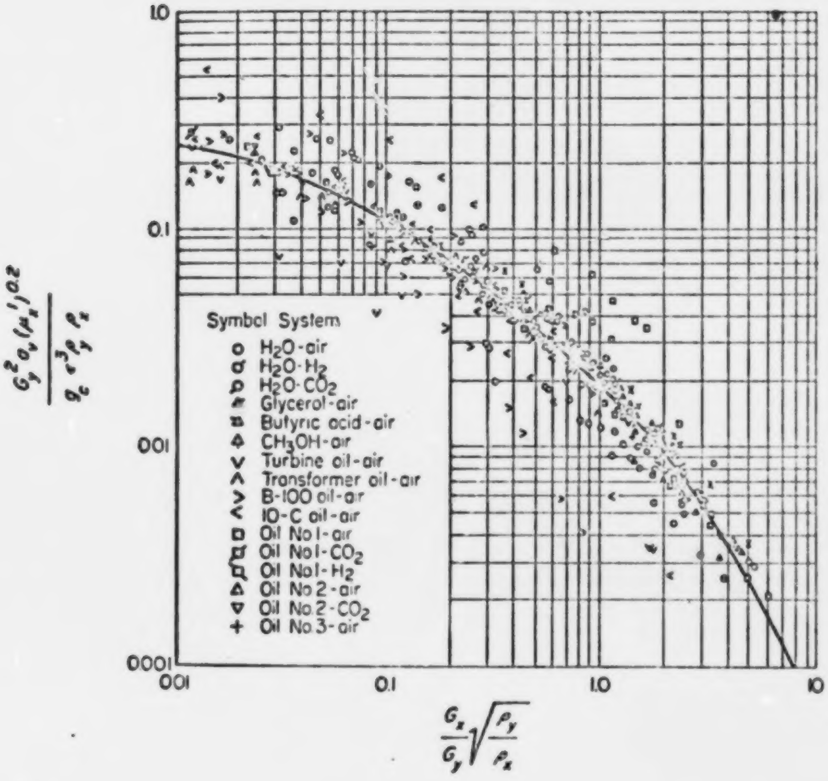


Fig. 30. Flooding velocities in packed tower (McCabe and Smith).[14]

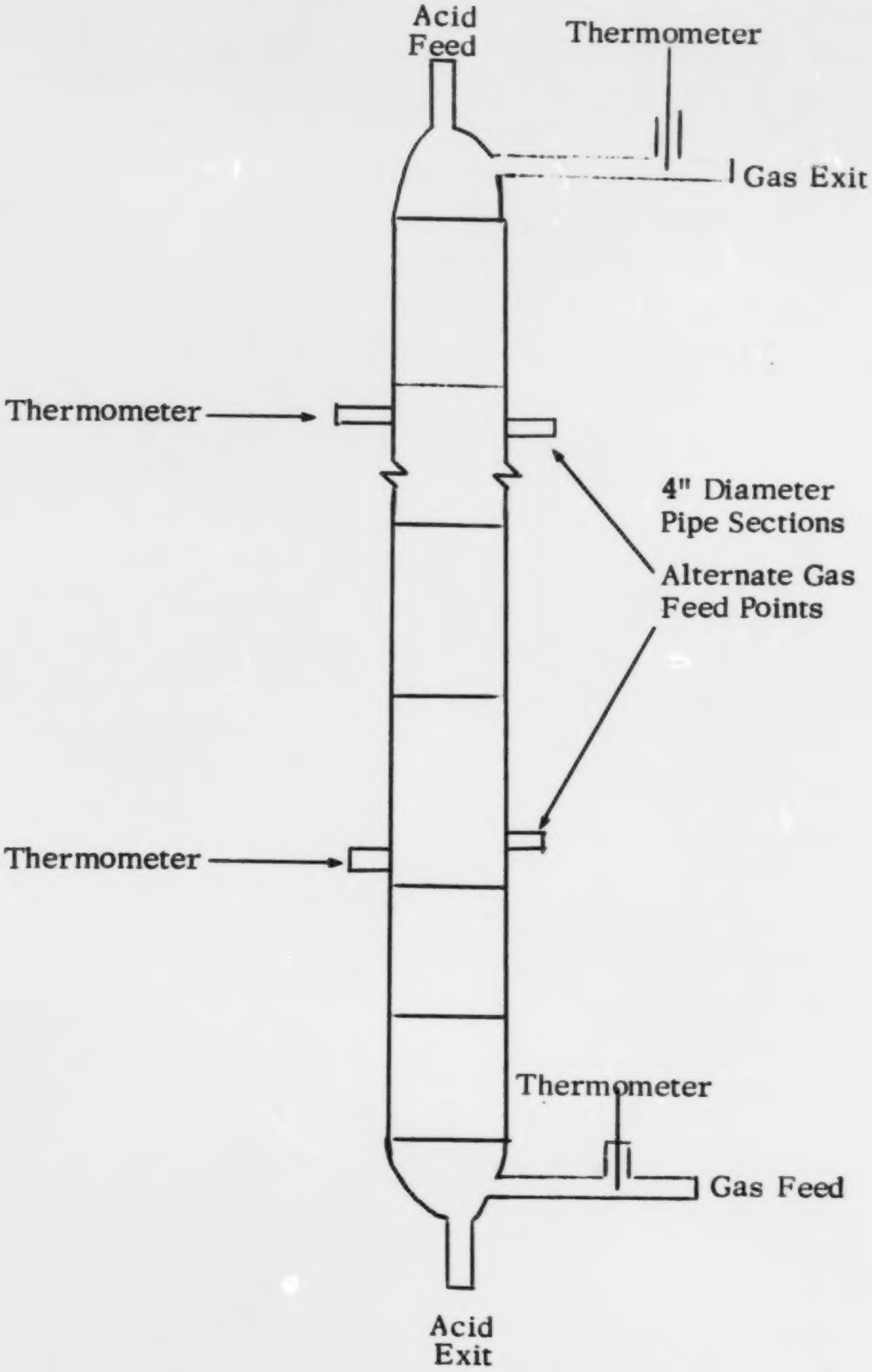

Acid Feed
Thermometer
Gas Exit
Thermometer
4" Diameter Pipe Sections
Alternate Gas Feed Points
Thermometer
Thermometer
Gas Feed
Acid Exit

Fig. 31. Scrubber

6) Stripper. The stripper is a packed column, also of 4 inch diameter and variable height. The 4 inch diameter is somewhat oversized for this equipment but will not cause any loss in efficiency and is being used to achieve plant simplicity by means of interchangeable parts. All piping will be 1 inch in diameter, while all process components will be 4 inches in diameter. This size is based on the optimization of the scrubber detailed in the previous section since it was considered that the scrubber was the critical component in the process. (If the scrubber does not work to maximum efficiency, pollutant gases will escape to the atmosphere.)

The stripper will be operated by passing hot gases countercurrent to the nitrose stream coming from the scrubber. The equilibrium data[4] indicate that in order to remove the N_2O_3 a large amount of water will also be stripped from the nitrose. This wet gas constitutes a recycle stream which adds a blower operating cost burden to the process. One of the tasks to be undertaken during the operation of the pilot plant is the development of methods either to remove this water from the recovery stream or to avoid its pickup in the first place.

The stripper and the NO reoxidizer will be set up on an experimental basis so that process modifications can be easily incorporated during the continuous operation of the pilot plant. The plant will be initially constructed so that the system can be operated continuously regardless of the efficiency of the stripper and the oxidizer. This means that steady state will be achieved in the reactor, the scrubber and the acid concentrator even if the nitrogen oxides are not being recovered and recycled efficiently.

7) Acid Concentrator. In order to recycle the acid used in the scrubber, it must be stripped of its oxides of nitrogen and concentrated back to 80%. Since the concentration of sulfuric acid is a well established process which does not need additional development at this time, we do have the alternative of dumping the acid, which amounts to about 7 gal/hr. Since this would be inconvenient as well as costly, a distillation column will be put in the system to concentrate the acid to the desired level. The

goal here is to make the pilot plant as complete and self-contained as possible. This will help in later evaluation of heat requirements, as well as enable us to introduce process modifications in a realistic manner.

The concentrator will be constructed of 4 in. Corning pipe, with a reflux head and condenser on top of a short packed distillation column. Figure 32 shows the setup of this apparatus.

The acid concentrator has been designed as a distillation column heated with electric heating mantles. The mantles will heat the cool feed (about 150°F) from the stripper (initially directly from the scrubber) and boil off sufficient water to increase the concentration to 80%. Based on a water input of 5% in the flue gas stream, a reactor inlet NO_2/SO_2 ratio of 2.0 and a scrubber L/G of 1.0 moles of acid per mole of flue gas, the liquid leaving the scrubber should have the following composition:

H_2O	23.7%
H_2SO_4	75.8%
N_2O_3	0.5%

On a basis of 10 SCFM of flue gas entering the system, the flow rate of liquid scrubber effluent would be 1.19 lb/min of acid with this composition. To increase the concentration to 80% acid, 0.0595 lb/min of water have to be removed.

In order to determine the amount of heat needed to remove this water, the enthalpy-concentration diagram shown in Fig. 33 was used. The technique used for determining the heat input is to subtract the enthalpy of the original solution from that of the total of the hot liquid and the vaporized water:

$$\Delta H = n_2 H_2 - n_1 H_1$$

$$H_1 = H_{(76\%\ H_2SO_4 \text{ at } 150°F)}$$

$$H_2 = H_{(80\%\ H_2SO_4 \text{ at } 395°F)} + H_{(\text{steam at } 395°F)}$$

$$n = \text{lb of material}$$

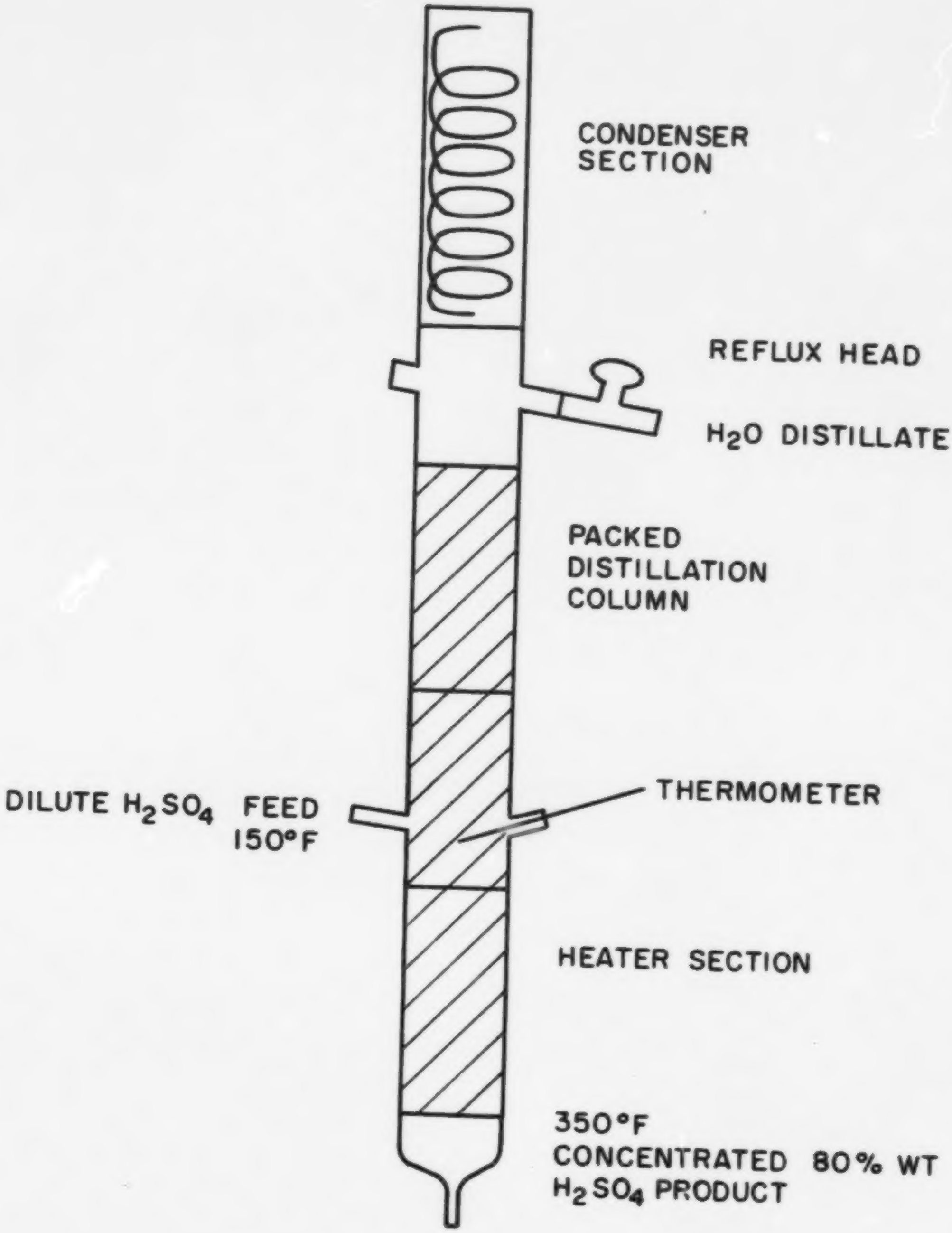

CONDENSER SECTION
REFLUX HEAD
H2O DISTILLATE
PACKED DISTILLATION COLUMN
THERMOMETER
DILUTE H2SO4 FEED 150°F
HEATER SECTION
350°F CONCENTRATED 80% WT H2SO4 PRODUCT

Fig. 32. Acid concentration

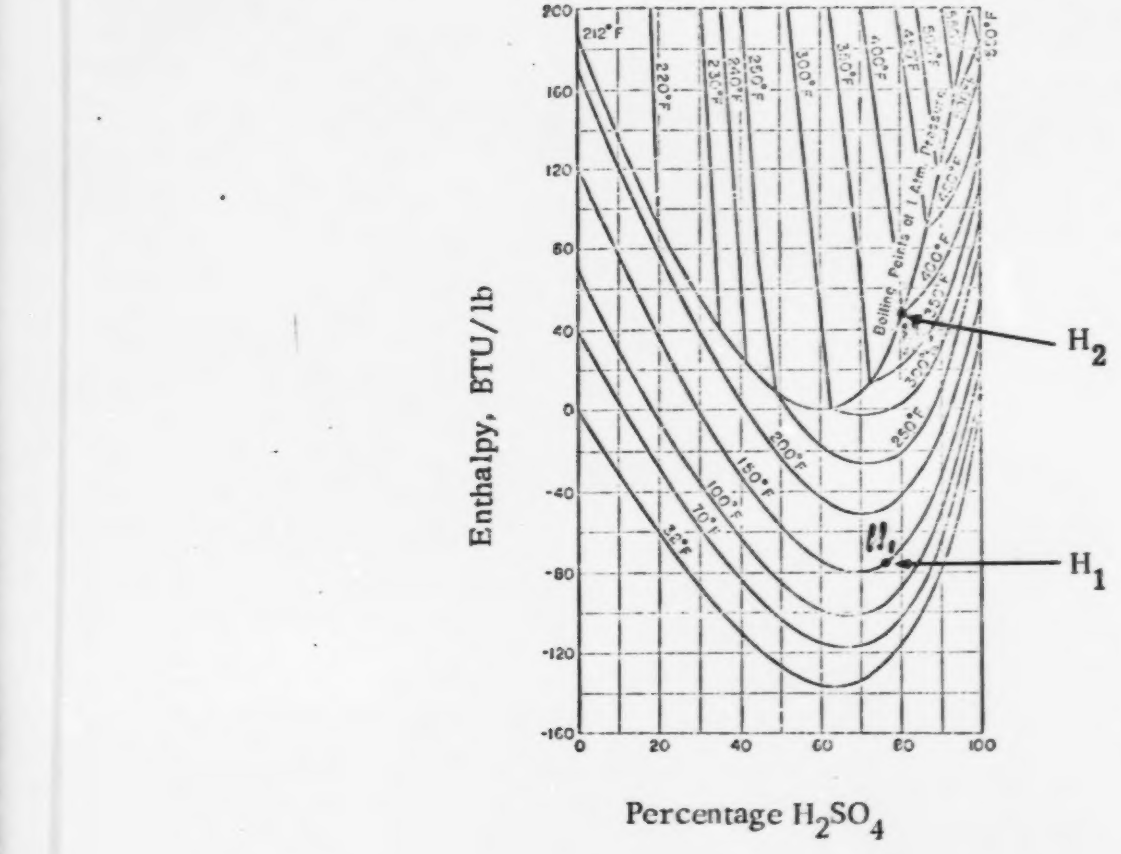


Fig. 33. Enthalpy-concentration diagram for aqueous sulfuric acid at 1 atm.[16] Reference states enthalpies of pure liquid components at 32°F.

The enthalpies of the sulfuric acid solutions are shown in Fig. 29 as H_1 and H_2. The enthalpy of the superheated steam is determined from standard steam tables.[17] The values for each are:

H_1 = −75 BTU/lb
H_2 (acid only) = 47.5 BTU/lb
H_2 (steam) = 1137.5 BTU/lb
n_1 = 1.19 lb/min (79% acid)
n_2 = 0.0595 lb H_2O/min + 1.13 lb/min (80% acid)

Calculating from these values, ΔH is 209 BTU/min or 3680 watts in equivalent electrical power. Using heating mantles along 28 inches of the 4 inch pipe that makes up the distillation column results in a heating requirement of 9.3 watts/in^2, well within the design capability of the heating mantles.

One aspect of the design of the concentrator system that must be considered is the heat transfer capability of the glass pipe. In other words, can the glass transfer the required amount of heat fast enough at a reasonable thermal gradient across the glass. To get an idea of this, the required gradient was calculated from the following equation:

$$Q = U A \Delta T \tag{1}$$

where

Q = heat transferred BTU/min
U = over-all heat transfer coefficient BTU/hr/ft^2/°F
A = surface area for heat transfer
ΔT = temperature gradient across the pipe

This equation is an oversimplification of the situation since the temperature gradient varies over the length of the heated section. It is more accurate to use the log mean temperature difference which is defined:[17]

$$\overline{\Delta t_L} = \frac{\Delta t_2 - \Delta t_1}{2.303 \log \left(\dfrac{\Delta t_1}{\Delta t_2} \right)} \tag{2}$$

Corning suggests using a value of 55 BTU/hr/ft^2/°F for the over-all heat transfer coefficient for glass heat exchangers with a cool liquid on one side and a condensing vapor on the hot side. That situation is more efficient than the conditions existing in the proposed acid concentrator where there is a liquid film on the cold side and the heating mantle (with an air space) on the hot side. From an examination of over-all heat transfer coefficients of other systems, an estimate of 35 BTU/hr/ft^2/°F is probably reasonable. The value of $\overline{\Delta t_L}$ was calculated from equation (1) using the following values.

$Q = 209$ BTU/min

$U = 35$ BTU/hr/ft^2/°F

$A = 395$ in^2 (28 inch mantle for 4 inch pipe)

The value of $\overline{\Delta t_L}$ is then 132°F.

The outside wall temperature can now be calculated from equation (2) if one assumes that the heating mantle temperature is constant along the length of the pipe, using 150°F for the inlet acid temperature and 395°F for the outlet temperature. Therefore, if T is the outside wall temperature:

$\Delta t_1 = T - 150$

$\Delta t_2 = T - 395$

Rearranging equation (2) and solving for T:

$$T = \frac{150 - 395\,C}{1 - C}$$

where

$$C = 10^{(245/2.303\,\overline{\Delta t_L})}$$

Substituting 132°F for $\overline{\Delta t_L}$:

$C = 6.42$

Substituting in equation (3):

$T = 441°F$

This means that in order to boil 1.12 lb/min of 75.8% sulfuric acid and concentrate it to 80% in a 28 inch long, 4 inch glass pipe, the outside of the glass pipe has to be maintained at 441°F. (This, of course, depends on the actual operating heat transfer coefficient. If in practice it is lower than the value used above, the pipe temperature will have to be higher.)

The recommended maximum operating temperature for the Corning pipe system is 450°F which is very close to the wall temperatures needed for evaporation of the water from the boiling acid. Upon consultation with Corning it appears that this maximum temperature is set for two reasons: (1) the maximum use temperature of the Teflon gaskets used at the flanged joints is 450°F and (2) the glass pipe is tempered at the ends to increase its strength where the stress on the flange is applied and also to maintain the roundness of the pipe under stress, avoiding high local stress concentrations in the pipe. Corning admits to being somewhat conservative in their temperature rating of this equipment and says that with care to avoid thermal shock, wall temperatures of 500°F can be tolerated. Thus it would appear that our system can be operated without serious problems.

There is another approach to this acid concentration problem which would avoid the use of the high pipe temperatures — run the distillation under vacuum. As the total pressure is reduced, the boiling point is also reduced, thus allowing us to concentrate the acid at lower temperatures.

Table XXI show vapor pressure data for water over sulfuric acid solutions at various concentrations and temperatures in the range of interest.

From the data in the table below, it can be seen that to lower the boiling point of the 80% sulfuric acid about 110°F, the pressure has to be reduced to 108.7 mm Hg. If heat is put in at the necessary rate, the vaporization process should take place fast enough to concentrate the acid to the desired level.

Table XXI. Vapor Pressure of Water Over Sulfuric Acid Solutions (mm Hg)[4]

Temperature (°F)	Acid Concentration		
	75.7% wt	78.0% wt	80.0% wt
140	4.9	2.9	1.7
158	8.7	5.2	3.4
176	14.7	9.3	6.5
194	24.3	15.6	11.5
212	39.1	25.6	18.8
230	60.3	40.9	30.9
248	91.4	63.7	48.0
266	134.6	95.9	72.6
284	144.2	141.3	108.7
370	760	—	—
385	—	760	—
395	—	—	760

The equipment that has been ordered can be easily adapted to operation under moderate vacuum and the heaters have been sized to provide more than enough heat to boil the acid at atmospheric pressure. This will allow a wide range of operating temperatures and pressures, giving us substantial versatility for acid concentrator performance. If there are difficulties with either of these two approaches to the concentrator, there are two other alternatives: preheating the acid feed, or using special Corning heat exchanger pipe which has an over-all heat transfer coefficient three times that of the standard Corning pipe (although it is not primarily intended for column use).

8) NO Oxidizer

The NO oxidizer will be a straight tube pipe reactor virtually identical to the SO_2 oxidation reactor shown in Fig. 25. The length will depend on the concentration of NO in the stripper gas and the required residence time for reoxidation to NO_2.

In the evolution of this process it has been found that there is essentially no advantage to using a $NO_2/NO/SO_2$ ratio of 3/1/1. The unit will work equally well with a mole ratio of NO_2/SO_2 of 2/1. Of course there must be a slight excess of NO_2 in order to assure the complete oxidation of SO_2, but the 200% excess discussed previously is probably unnecessary. Some adjustment in mole ratio will be required since it is impractical to assume that all the NO from the stripper will be oxidized to NO_2 and some reasonable level of reoxidation will have to be planned, e.g. 90%. There will then have to be an excess of NO_2 to permit the mole ratio of NO_2/NO to be 1/1 as the gas enters the scrubber. These two requirements for slightly higher NO_2 levels than would be assumed theoretically would probably be satisfied by a 10-20% excess of NO_2 in the recycle stream.

9) Pumps

The two important criteria in selecting pumps for sulfuric acid service are flow capacity and materials of construction. Considerations such as suction head, discharge head, horsepower and uniformity of flow (pulsations) are only of secondary importance.

The capacity of the pump has to be in the 0.1 -0.2 GPM range, thus establishing the requirement for a metering pump with a capability for carefully controlled flow. This feature is quite important since the efficient operation of the system depends on the ability to balance the material flows in each stage of processing.

The materials of construction depend on the temperature of the acid being pumped, which of course depends on the process stage in question. An examination of Fig. 27 reveals that three pumps will be used in the system. The acid leaving the scrubber will be relatively hot. If the scrubber inlet acid is at 80°F, the diluted acid which is to be pumped to the stripper will pick up sensible heat from the reacted flue gas and heat of solution from reaction with the water, thus leaving it at about 275 °F. The acid leaving the stripper will be somewhat hotter, depending on the temperature of the stripping gas and the flow ratio of gas to acid. Temperatures will probably be in the 285-300 °F range. It is the acid leaving the concentrator that will be the hottest. This acid will be at its boiling point which is 395 °F for 80% acid.

Examination of corrosion tables indicates that the only materials which have adequate service lives for 80% sulfuric acid above 200 °F are high silica iron (known by the trade name of Duriron), glass, platinum, gold and tantalum. The last three are out of the question because of price, which leaves glass and Duriron as the only possible materials. An extensive search of the industrial literature indicates that there are no metering pumps made of Duriron and the glass metering pumps that are available have thermal shock problems that restrict their use to temperatures below 150 °F. Since Duriron is not machinable, it will be difficult if not impossible to obtain a custom-manufactured pump out of this metal, which leaves only one solution — the acid which leaves all three stages will have to be cooled before it is pumped. (It should be noted here that for the higher flow rates that will be present in larger scale plants, Duriron pumps of the proper size are readily available.)

For acid temperatures below 200° F, pumps are readily available in the desired flow range. Carpenter 20 stainless steel is recommended for use with 80% sulfuric acid up to about 200° F, and the pumps that will be used have the following specifications:

Mark II Chemical Metering Pump (Clark-Cooper Co.)

Liquid end	Carpenter 20
Pump housing	Cast iron
Plunger	Carpenter 20
Check balls	Ceramic
Seals	Teflon
Packing	Teflon/asbestos
Speed	88 strokes/minutes
Flow rate	0 - 0.175 GPM

10) Flow Meters

There are essentially three different types of flow meters in the system: gas service in the 10 SCFM range, gas service in the 0. 1 SCFM range and liquid in the 0. 1 GPM range. The meters were chosen on the basis of ease of operation and compatibility with the rest of the system.

Several companies make flowmeters of the glass rotameter variety, and they are all about the same in price and operational features. Only one company, however (Schutte and Koerting Co.) makes their flowmeters compatible with Corning Conical Pipe. It is possible, of course, to use standard threaded connections which are cheaper, but the connection to the glass pipe has to be made somewhere and the adapters necessary make the total cost relatively close. The convenience of using the same type of connectors compensates for the additional cost.

Concerning the sulfuric acid service, there was an alternative of either calibrating the metering pumps or using flowmeters. While it is likely that the pumps can be calibrated, it is felt that this would involve a somewhat indirect control method and slow changes in pump performance could not be determined. A situation which would require occasional pump recalibration would be impractical. There was also a choice of using one acid flowmeter and valving it so that all three process streams could be monitored individually. It turns out that the pipe and valves would cost as much as the additional meters (aside from the contamination problem while switching from one stream to another). The decision was made to buy three meters, one for each acid stream.

11) Heating Mantles

There will be several places in the system that will require heating because of process requirements or because the mini-plant will have higher heat losses than an actual plant and will need reheating. The acid concentrator, which is a distillation column, will need a heated section at the bottom to act as a reboiler. The scrubber will probably need some heated sections to compensate for heat losses, as will the stripper. There may also be a need to reheat the sulfuric acid after it is pumped.

There are two ways to perform these reheating operations: run the process streams through heat exchangers or use external heaters. In the case of the scrubber and the stripper there is really no choice, and heating mantles will be used. Although this technique is somewhat more expensive than using heating tapes, the mantles provide more uniform heat and are much easier to use since they will not require additional insulation after they are installed.

Since the entire system is designed in a modular fashion using short sections of 1 and 4 inch pipe, the heating mantles will be obtained in the same way. By this technique the mantles can be purchased without designing special shapes or sizes and can be used where needed. The mantles will be obtained from Glas-Col Company.

12) Construction and Start-Up

The pilot plant was constructed in the general manner shown in Fig. 27 using the Unistrut framework system for support. No problems were incurred in the construction aside from the usual equipment delivery delays and the final system is shown in the photograph in Fig. 34.

A significant problem arose when the plant was started up. There was a considerable pressure drop across the reactor and scrubber. The pressure drop was too high to be overcome by the natural convection gas burner being used. Table XXII presents the back pressure of the system at various gas flow rates with the scrubber dry. (The "system" for these tests included the 10 cfm flowmeter, the SO_2/NO_2 reaction chamber, the scrubber-packed with 8.5 ft. of 3/8 in. Intalox saddles, nine elbows, four thermometer well constrictions and thirteen feet of 1 inch glass pipe.)

Table XXII. Experimentally Measured Gas System Pressure Drop as a Function of Gas Flow Rate

Gas Flow Rate (cfm)	Pressure Drop (Inches of Water)
2. 8	2. 0
3. 7	3. 0
4. 7	4. 5
5. 7	6. 5
6. 8	8. 5
7. 8	10. 8
8. 9	13. 5
10. 0	16. 0

Data supplied by U. S. Stoneware indicates that the column would have a pressure drop of 0. 3 inches of water per foot of packing when operated dry and about 0. 4 inches of water when operated at an L/G ratio of 2. 0 and a gas mass velocity of 600 $lb/ft^2/hr$ (10 cfm in a 4 inch column). The

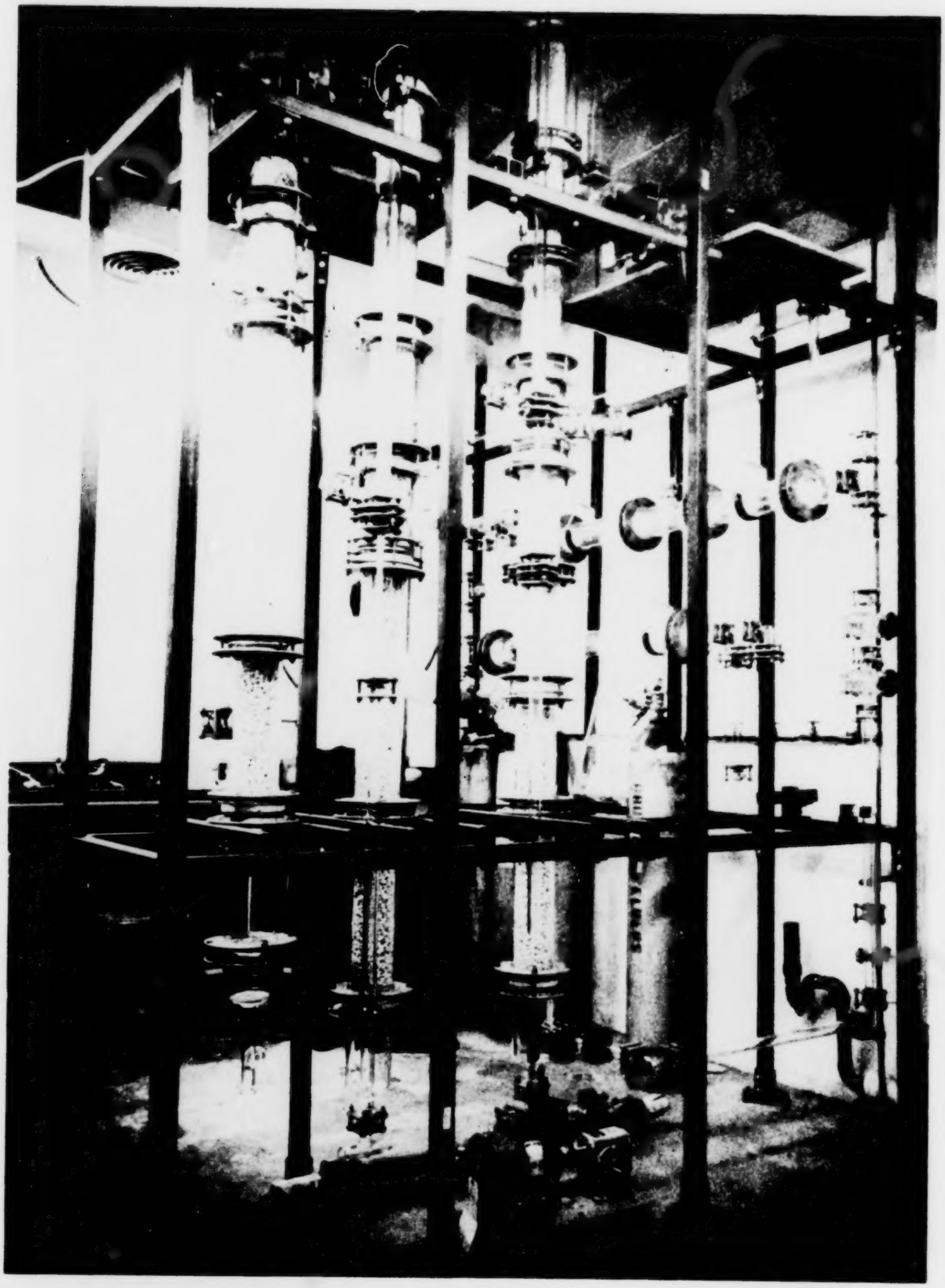


Fig. 34. Pilot Plant

difference of 0. 1 inches of water per foot of packing results in a correction of about 1 inch of water additional pressure drop at 10 cfm when the acid is flowing through the column. Actual measurements of pressure drop in the dry column show a drop of less than 2 inches of water instead of the 2. 4 predicted which suggests that 1 inch additional pressure drop should be more than enough to correct for liquid flow.

This total pressure drop of about 17 inches of water is less than the drop experienced with the small 1. 0 cfm bench scale system used in earlier studies, which is probably due to proper sizing of pipes and fittings (the old set-up used some small-bore fittings which undoubtedly contributed a large portion of the pressure drop). However, this pressure drop is still too high to allow a natural draft to be formed in the gas burner.

There were several ways to approach the pressure drop problem and the following were considered:

1. pressurized gas burner... There are commercially available gas burners which mix the air and the gas and force-feed the mixture to the burner under pressure. In general these devices have relatively low operating pressures and are fairly expensive.

2. vacuum exhaust... The vent from the scrubber could be fed into a vacuum pump which would pull the gases through the whole system. This would be relatively simple to install and only moderately expensive.

3. in-line fan... The exhaust gas from the gas burner could be fed to an in-line fan which would force the gases into the processing system. The gases would have to be cooled before they reached the fan in order to simplify the fan design. This approach is straightforward, but would involve modifications in the fan and the piping since these devices are not usually designed for operation with small bore piping systems.

The system decided on what was a moderately high pressure in-line blower which takes the output of the gas burner at about 250° F and forces it into the system. The blower has a maximum exit temperature of 350° F and since the blower itself heats the gas it is necessary to introduce a relatively cool gas. The blower was installed and appears to have solved the back pressure problem.

13) Initial Experimentation

Initial runs on the pilot plant were aimed at evaluating the scrubber efficiency for removing both sulfur dioxide and nitrogen oxides. The reactor was heated to 300° F and an artificial flue gas at 10 SCFM containing about 0.3% SO_2 and 1% water was used as the feed stream. No effort was made to use the proper amount of water in the gas because the whole system was not going to be tested and it was therefore not essential to have any more water than the minimum necessary to make the acid. The flue gas was mixed with NO_2 in various NO_2/SO_2 ratios and the reacted gas stream fed to the scrubber. The scrubber acid was fed at an L/G of about 1.0 mole/mole and a temperature of 90° F. The gas was sampled after the scrubber and was analyzed by infrared absorption for oxides of nitrogen and sulfur dioxide. The effluent acid was analyzed for its nitrosylsulfuric acid content by $KMnO_4$ titration.

Table XXIII shows the results of a number of experiments where the NO_2/SO_2 ratios were varied from about 4 to 2. In all cases the SO_2 was completely absorbed, but as would be expected, the NO_2 absorption depended on how much excess NO_2 was present above that required to form an equimolar $NO:NO_2$ mixture after the SO_2 oxidation reaction.

Examination of the data shows that the amount of nitrogen oxides absorbed in the scrubber was usually about twice the amount of sulfur dioxide in the feed stream. Since no SO_2 was apparent in the exit gas, it appears that the NO_2 oxidized all of the SO_2 forming enough NO to allow the absorption of an equal amount of NO_2, both being equal to the original amount of SO_2 present in the gas.

Table XXIII. Experimental Results: Pilot Plant

Entrance Gas Partial Pressure (torr)		Scrubber Exit Gas Partial Pressure (torr)*		% $HNSO_5$ in Scrubber Outlet Acid	Scrubbing Efficiency % NO_x Removal†	Material Balance Error‡ %
SO_2	NO_2**	SO_2	NO_2			
2.28	9.45	<0.01	5.0	**1.28**	47	10.0
2.80	9.45	<0.01	4.1	**1.63**	57	9.1
2.80	7.85	<0.01	2.4	**1.95**	70	4.2
2.80	7.48	<0.01	1.9	**2.00**	75	4.0
2.80	6.63	<0.01	1.52	**2.18**	77	-10.2
2.80	5.74	<0.01	0.07	**1.78**	98+	16.6
2.80	5.74	<0.01	0.08	**2.01**	98+	6.2
2.80	5.74	<0.01	0.08	**1.98**	98+	7.6

*NO could not be measured in the effluent gas, because by the time the gas was analyzed (infrared) all the NO was oxidized to NO_2. Therefore, total NO_x only was measured.

† Based on inlet and outlet NO_x concentrations in the gas.

‡ Conditions: $$\frac{NO_x\ (in) - NO_x\ (out)}{NO_x\ (in)} \times 100$$

** No NO was added to reactor inlet gas.

L/G = 1.0 mole/mole

Scrubber inlet acid temperature = 90° F

Gas flow rate = 10 SCFM (1% H_2O)

Acid flow rate = 0.085 GPM (80% H_2SO_4, 0% $HNSO_5$)

Reactor inlet gas temperature = 300° F

Good material balance closure was obtained in all the runs with the error being less than 10% in all cases. The experimental conditions are very close to those in the standard Lead Chamber Process, which has been used for more than a century, and the results agree with Lead Chamber Process commercial operating data. It is clear that control of the NO_2/NO ratio is vital to achieve high enough NO_x absorption to make the process profitable.

K. Process Improvements (Bench Scale)

1) General Approach to Process Modification

Examination of the schematic of the Modified Chamber Process in Fig. 20 and the heat and material balances for the process in Tables XI and XII reveals that the required 37% excess heat discussed in Section V-H9 is divided approximately in half between the stripper and the acid concentrator. This means that half the heat is needed to remove the excess water absorbed by the acid in the scrubber and the other half needed to concentrate the N_2O_3. The basic approach to the heat requirement problem then, was to 1) try to prevent the water from being absorbed in scrubber, and 2) find another way to concentrate the N_2O_3.

2) Reactor Gas Condensation

Initial work in trying to prevent the water from being absorbed in the scrubber acid was to remove the water from the flue gas stream before it got to the scrubber. It was thought that by cooling the gas between the reactor and the scrubber, enough water could be condensed so that the scrubber acid would not be excessively diluted. For instance, if the partial pressure of water in the flue gas stream were reduced from 50 torr (about 7%) to 27 torr (3.5%) by cooling the gas to 90 °F, thus condensing out the water as dilute sulfuric acid, then the acid in the scrubber would be diluted to only about 78% instead of 76% as previously. Then when the acid was heated in the stripper, the excess water would be removed along with the N_2O_3 and recycled to the reactor with the concentrated N_2O_3. Then the water would continue back to the condenser where all the water in excess of 3.5% would drop out. By this method the flue gas entering the reactor is enriched with water, but loses everything down to 3.5% in the condenser. At steady state, flue gas containing 3.5% H_2O enters the scrubber and a constant amount of water is recycled from the stripper. The diluted acid from the condenser would be concentrated and sold and since this is a relatively small amount of acid compared to the large amount of recycle acid, the heat requirement should be considerably reduced.

This scheme was tried experimentally by running the reacted flue gas into a condenser and analyzing the effluent liquid and gas as shown in Fig. 35. The nitrogen (at room temperature) was bubbled through a water pre-saturator, with the water temperature being 113 °F. This would provide a water content of about 9% in the gas if it came to equilibrium, but there was sufficient cooling of the gas before it entered the reactor that it was highly probable that the actual concentration was much lower. Other methods were used to determine the water content of the reactor inlet gas accurately and these will be mentioned later.

The reactor tube was wrapped with electrical heating tape, with the heat input being that which would provide an exit gas temperature of 300 °F at the thermocouple. Since the gases entered at a much lower temperature, there was a temperature gradient along the reaction tube.

The hot reacted gases passed into the coils of a condenser. The shell of the condenser contained circulating cooling water that was kept at constant temperature in an external thermostated bath. The water flowed through the condenser at such a rate that the exit and entrance temperature of the water was about the same. This created a constant temperature region along the length of the condenser.

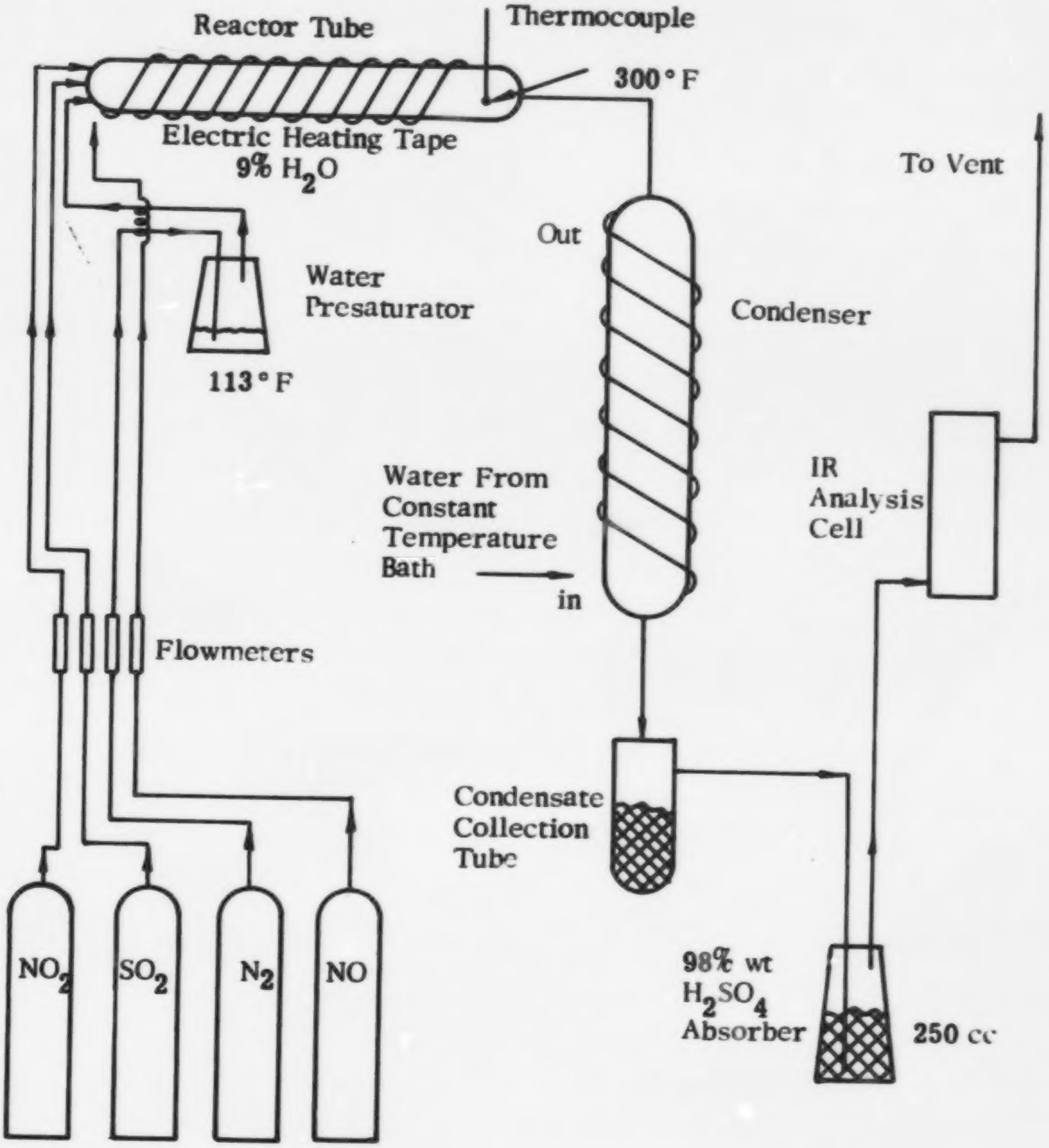

Reactor Tube
Thermocouple
300 °F
Electric Heating Tape
9% H_2O
To Vent
Out
Water
Presaturator
Condenser
113 °F
Water From
Constant
Temperature
Bath
in
IR
Analysis
Cell
Flowmeters
Condensate
Collection
Tube
NO_2
SO_2
N_2
NO
98% wt
H_2SO_4
Absorber
250 cc

Fig. 35. Experimental apparatus for H_2O condensation experiments

The gases and the condensate passed into a collection tube, with the gases being piped out into an absorber containing 98% sulfuric acid. After passing through an infrared analytical cell, the gas was vented to the atmosphere. The purpose of the sulfuric acid absorber was to remove all the sulfuric acid mist and water from the gas before it went through the IR cell. This cell contains sodium chloride windows which would have been affected by the aqueous vapors in the gas stream. The acid would absorb water, acid mist and equimolar quantities of nitric oxide and nitrogen dioxide but would not collect sulfur dioxide and excess nitrogen dioxide in significant quantities. Thus a complete nitrogen oxide balance could be made by analyzing the absorber acid for nitrosylsulfuric acid and the gas for both NO and NO_2. The amount of water in the gas was determined from the increase in volume of the absorber acid during the experimental run (assuming 0% H_2O in the vent gas). A complete sulfur balance could be made if it were possible to analyze the absorber acid for sulfuric acid content, but the large volume of acid required to provide a constant rate of absorption of the oxides of nitrogen over a period of time made it impossible to detect the pickup of very small quantities of sulfuric acid. It was necessary to absorb the nitrogen oxides over a significant period of time in order to develop a high enough concentration of nitrosylsulfuric acid to allow accurate analysis.

The only parameter that was varied during the experimentation was the temperature of the circulating water in the condenser. The other conditions were maintained as follows:

Nitrogen flow rate	28, 300 cc/min (1 cfm)
Sulfur dioxide flow rate	85 cc/min
Nitrogen dioxide flow rate	230 cc/min
Nitric oxide flow	85 cc/min
Water presaturator temperature	113 °F
Reactor gas temperature	300 °F
Reactor retention time	0.46 sec (assuming an average reactor temperature of 185 °F)

In addition, the residence time in the 98% H_2SO_4 absorber was maintained at about 30 minutes with the sulfuric acid volume in the absorber being about 250 cc (both were determined exactly for each experiment). The results of the initial condensation experiments are shown in Table XXIV.

At 140° F there was virtually no condensation, although this is below the sublimation temperature of nitrosylsulfuric acid and we might have expected to see crystals forming on the condenser walls. There was some fogging of the condenser coil, but nothing could be collected. These results verify earlier experiments which demonstrated the futility of trying to condense solid nitrosylsulfuric acid. (After the experimentation was completed, it was observed that crystalline material had formed in some liquid puddles in the reactor. This was undoubtedly nitrosylsulfuric acid, but in small quantities and difficult to collect.)

At 122° F there was somewhat more condensation, but it still could not be collected. It was not until the condenser temperature was dropped to 104° F that appreciable condensate was formed. This material was collected and analyzed for both acid content and the presence of nitrogen oxides. As the table shows, the solution was 49% H_2SO_4 in this case, while the nitrosylsulfuric acid content was negligible. When condensation was performed at 86° F, the amount of condensate increased, as might have been expected, and the acid content decreased to 45%. Again there was negligible nitrosylsulfuric acid present.

Material balance concentrations showed that the acid collected in the two low temperature condensation experiments was only about 25% of the acid which had been formed in the reaction. This points out the well-known difficulty of removing sulfuric acid mists from gas streams. (It is assumed that the remaining 75% was absorbed in the H_2SO_4 absorber.)

It is interesting to note that the amount of N_2O_3 retained by the sulfuric acid in the absorber decreased as the gas temperature increased, although nitrosylsulfuric acid is more soluble in sulfuric acid at higher temperatures. This is partly due to the higher N_2O_3 vapor pressure at

Table XXIV. Results of Condensation Experiments*

Condenser Water Inlet Temp (°F)	Duration of Run (min)	98% H_2SO_4 Absorber			Exit Gas Concentration (mm Hg)			NO_x* Material Balance Error (%)	Final Volume of Condensate (cc)	H_2SO_4 Concentration (% wt)
		Final Acid Volume (cc)***	Water Pickup (cc)	Total N_2O_3 in Acid (g moles)	NO	NO_2	SO_2			
86	30	260	10	0.103	0.7	4.0	1.2	-1.4	2.1	45
104	30	266	16	0.087	0.7	4.2	1.1	0.0	1.8	49
122	30	275	13	0.081	0.7	4.2	1.2	3.1	<0.5	--
140	31	273	--	0.071	1.8	3.0	1.4	7.2	0	--

* Conditions -- See page 113

$$* \frac{NO_x \text{ (in)} - NO_x \text{ (out)}}{NO_x \text{ (in)}} \times 100 = \text{Error}$$

***Initial H_2SO_4 volume = 250 cc

higher temperatures and partly due to the shorter contact time of the gas in the acid since the gas volumetric flow rate was higher at the higher temperature.

One of the most significant results of the experimentation was the excellent reproducibility and reliability of the analytical procedures. Since the reactor conditions were the same in all four experiments, one would expect that the exit gas would have the same composition in all cases. For the most part this is true, with the exception being the 140° F condensation which was the first run made. This run is hard to explain, but even here the total material balance on the nitrogen oxides was closed to within 7.2%. It is interesting to note that the NO_x content of the exit gas was essentially constant even in this case although the NO/NO_2 ratio varied.

From the quantity of water picked up in the acid absorber, it is possible to determine the actual water content of the original gas stream. All the water in the gas stream was trapped in the acid scrubber since the IR analysis of the exit gas did not show any traces of water in any of the experiments. From the data in Table XXIV it can be calculated that the gas contained 2% water on the average. The reasons that the gas did not contain the anticipated 9.5% are that (1) the residence time of the gas in the presaturator was too short to allow the gas and liquid to come to equilibrium and (2) the gas cooled down after it left the presaturator and before it entered the reactor, thus allowing condensation of some of the water. In any case there was more than enough water in the gas to provide for the formation of sulfuric acid, and the low water content had no effect on the results. Since it was found that a portion of the acid condensed with the water making a dilute acid (about 45%) it was possible that the product could be concentrated to a usable level and thus partially solve the water problem. However, the difficulties in cooling the gas to these low temperatures (86-104° F) and recovering the acid mist made the technique impractical and the work was discontinued.

The experimental set-up used for the condensation experiments provided an opportunity to perform a valuable kinetic study on the sulfur dioxide oxidation reaction. Previous experimentation had shown that better than 90% of the SO_2 could be oxidized in less than 5 seconds contact time with the NO_2, but it was never clearly defined as to how much less could be tolerated. The gas phase material balance on the condensation experiments revealed that only about 40% of the SO_2 reacted during 0.46 seconds; obviously an insufficient amount of time being allowed for the reaction. It was decided to evaluate the kinetics of the SO_2/NO_2 oxidation reaction:

$$NO_2 + SO_2 \xrightarrow[H_2O]{} NO + SO_3$$

Two additional experiments were performed using the condensation apparatus where the residence time in the reactor was first doubled (0.92 sec) and then doubled again (1.84 sec), with all exit streams being analyzed as before. The results are shown in Table XXV and compared with the data from the 104°F experiment shown in Table XXIV.

Table XXV. Results of Kinetic Experiments ~~(104 °F)~~ 300°F

$$NO_2 + SO_2 \xrightarrow[H_2O(g)]{} SO_3 + NO$$

Reactor Residence Time (sec)	Duration of Run (min)	SO_2 Concentration in Exit Gas (mm Hg)**	% SO_2 Reacted
0.46*	30	1.15	43.6
0.92	60	0.80	60.8
1.84	90	0.40	80.4

* This run from Table XXIV

** SO_2 inlet concentration = 2.2 mm Hg.

These two additional experiments were carried out under the same conditions as the previous condensation one, with the gas composition being the same and the condenser again being operated at 104 °F. (The condenser was not really necessary for these experiments, but it was decided not to change the conditions.) The retention time was changed, but the total volume of gas passed through the absorber was kept constant in order to be able to analyze solutions of similar concentrations.

The data in Table XXV show that the SO_2 concentration in the exit gas decreased as the retention time increased, a not unexpected result. From this data we can calculate the reaction rate constant for these conditions. For the general reaction:

$$A + B \rightarrow \text{Products}$$

where a and b are the initial concentrations of A and B respectively, and the reaction rate is proportional to the concentration of both reactants, we can write the following general equation for the rate of reaction:[11]

$$\frac{dx}{dt} = k\,(a - x)\,(b - x)$$

with x being the decrease in each concentration after time t. This can be integrated using the boundary condition that x = 0 when t = 0:

$$t = \frac{2.303}{k\,(a-b)} \log \frac{b\,(a-x)}{a\,(b-x)} \qquad (4)$$

k, the reaction rate constant, can be determined by plotting t versus

$$\frac{2.303}{a-b} \log \frac{b\,(a-x)}{a\,(b-x)} \equiv \alpha$$

for several values of t, or k can be calculated directly for each case. This was done for the three sets of data shown in Table XXV. The calculations and results are summarized in Table XXVI.

Table XXVI. Calculated Reaction Rate Constant for SO_2 Oxidation by NO_2

t (sec)	a (SO_2) (torr)	b (NO_2) (torr)	x (torr)	α*	k
0. 46	2. 04	5. 5	0. 89	0. 115	0. 250
0. 92	2. 04	5. 3	1. 24	0. 206	0. 224
1. 84	2. 04	5. 3	1. 64	0. 386	0. 210

$$^{*}\alpha = \frac{2.303}{(a-b)} \log \frac{b(a-x)}{a(b-x)}$$

Figure 36 shows a plot of t versus α. The slope of the line gives the value for k of 0. 196. (Since the graph was plotted as $\alpha = kt$ the slope gives k directly rather than 1/k.)

Although the data falls on a perfect straight line, there is a slight error since the line does not pass through the origin. This accounts for the difference between the slope and the calculated values of k. The results are good enough to allow comparison with published values of k for this reaction. The most complete study of this reaction was done by I. N. Kusminych, E. J. Turchan and M. S. Archipowa who determined values for k at several concentrations and a range of temperatures.[18] Their temperature correlation of k is shown in Fig. 37.

From the Kusminych data it would appear that k should be 0. 372 at 300 °F rather than the 0. 196 found in our study. An examination of the reaction chamber in Fig. 35 will reveal the source of this discrepancy. Our apparatus was set up with the gas entering the heated

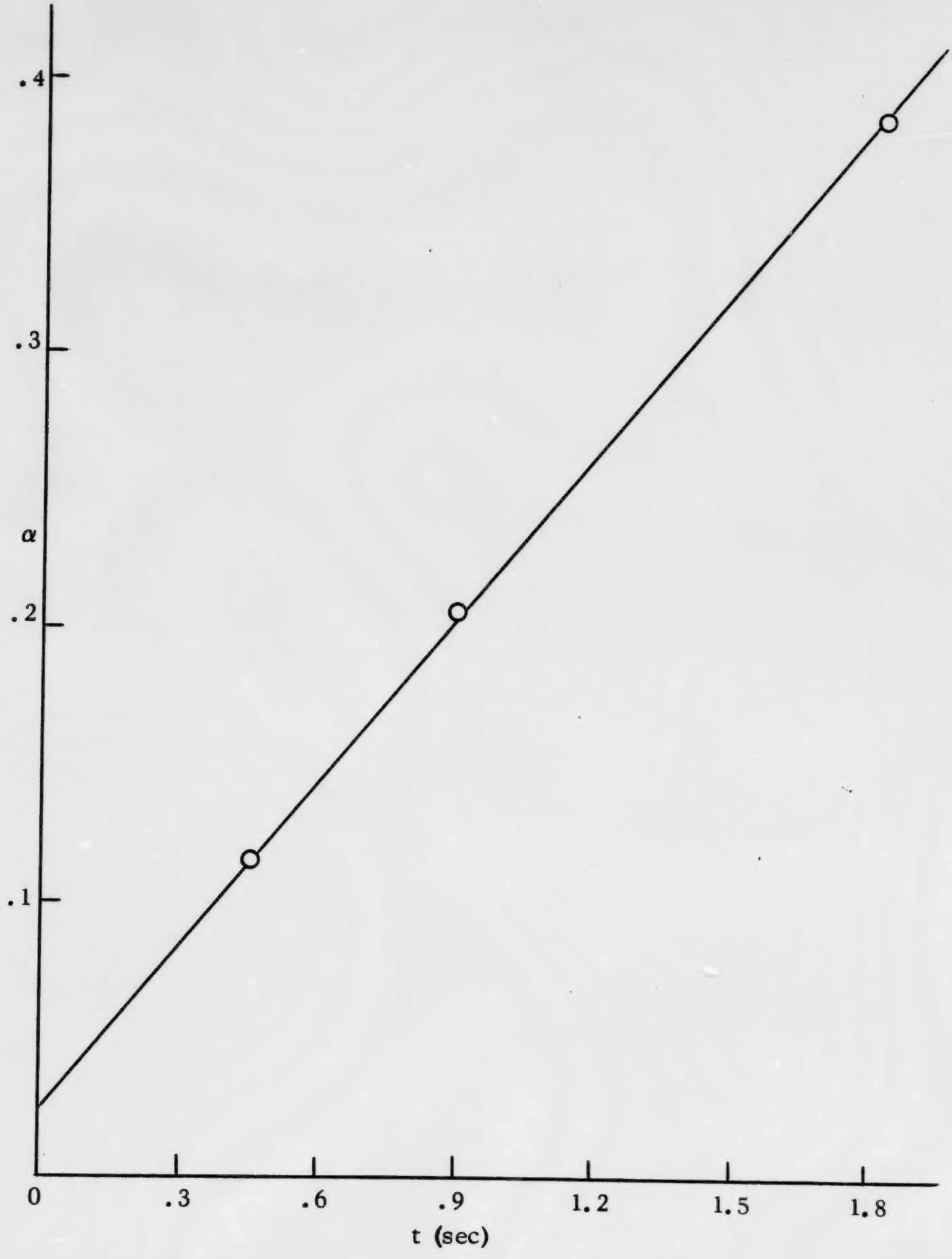


Fig. 36. α vs t for Reaction $SO_2 + NO_2 \rightarrow SO_3 + NO$

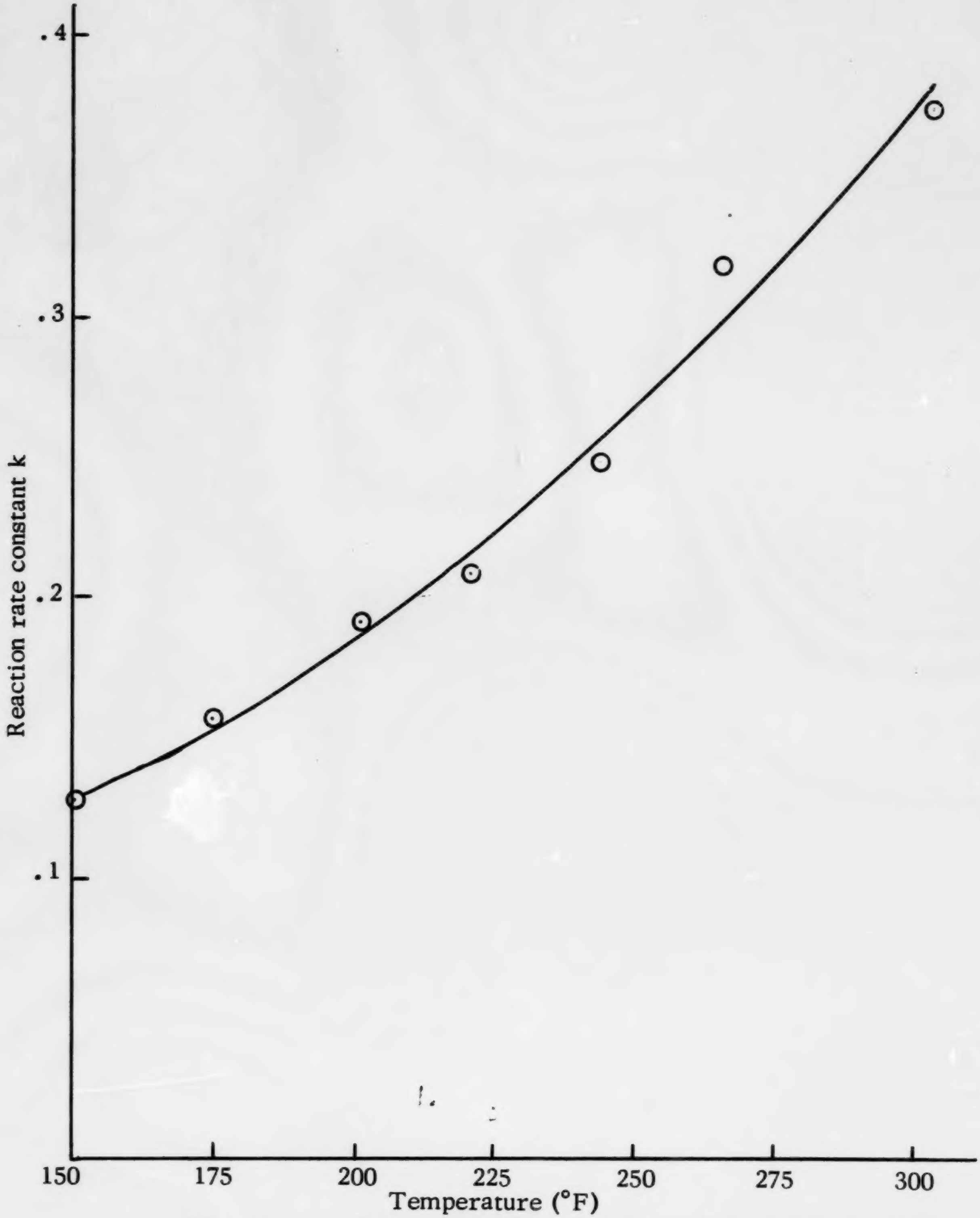


Fig. 37. Reaction Rate Constant as a Function of Temperature (Data of Kusminych, Turchan, and Archipowa)[6] for Reaction: $SO_2 + NO_2 \rightarrow SO_3 + NO$

reactor at about room temperature. Since the reactor heater was set so that the exit temperature was 300 ° F, there had to be a temperature gradient along the length of the tube. With the heat being introduced by a heating tape, it is possible to approximate the temperature profile of the reactor by a straight line relationship. This means that the resultant k should be representative of an over-all reaction at a linearly averaged temperature. From Fig. 37 it can be seen that a k of 0.196 is representative of this reaction occurring at a temperature of 210 ° F. The linear average of the temperature gradient in the reactor would be 185 ° F. We can interpret this difference as either a nonlinear temperature profile along the length of the reactor or a nonlinear relationship between temperature and reaction rate. In either case the agreement between the two is good.

Using the data of Kusminych and equation (4), it is possible to calculate the theoretical retention time necessary for 90% reaction at a constant temperature of 300 ° F. With a k value of 0.37 and initial concentration of 2 mm Hg of SO_2 and 6 mm Hg of NO_2, it would take 1.32 sec to achieve 90% reaction. If the NO_2/SO_2 ratio were reduced to 2/1 instead of 3/1, it would take 2.3 sec to achieve the same goal. These residence times are within the capability of the pilot plant reactor system.

3) High Temperature Scrubber

The concept of the high temperature scrubber as described in Section IV-D is based on the idea of maintaining the scrubber at a temperature such that the vapor pressure of water over the entering acid was equal to the partial pressure of water entering with the flue gas. (See Table XXI for water vapor pressure data.) By this technique all the water entering with the flue gas would leave with the clean stack gas and the acid would not be diluted. The primary question was whether or not the hot acid would absorb the oxides of nitrogen at these temperatures and thus keep the N_2O_3 losses to acceptable level.

In order to develop reasonable design criteria for a scrubber of this type, an analysis of the absorption capabilities of the system was conducted using the McCabe-Thiele method.[14] The following is a brief development of the method and the results for the system under consideration.

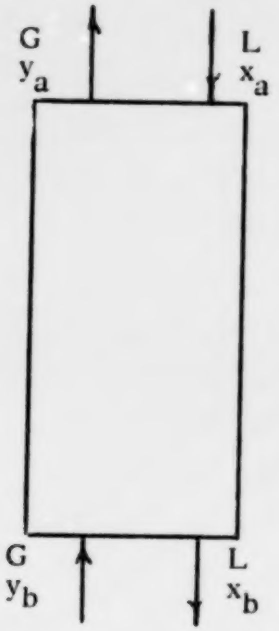


Fig. 38. Absorption column (NO_x Scrubber)

In considering the absorption of a gas in a liquid in a counter-current scheme as shown in Fig. 38, it is possible to predict absorber performance using the McCabe-Thiele method. An equilibrium line is plotted as shown in Fig. 39, and an operating line is determined by the terminal conditions of the column. The lower end of the operating line represents the conditions at the top of the column, and the upper end, the bottom of the column.

A material balance can be taken around the column using the following notation:[14]

x_a = solute concentration in the inlet liquid
x_b = solute concentration in the effluent liquid
y_a = solute concentration in the effluent gas
y_b = solute concentration in the inlet gas
L = liquid mass flow rate
G = gas mass flow rate

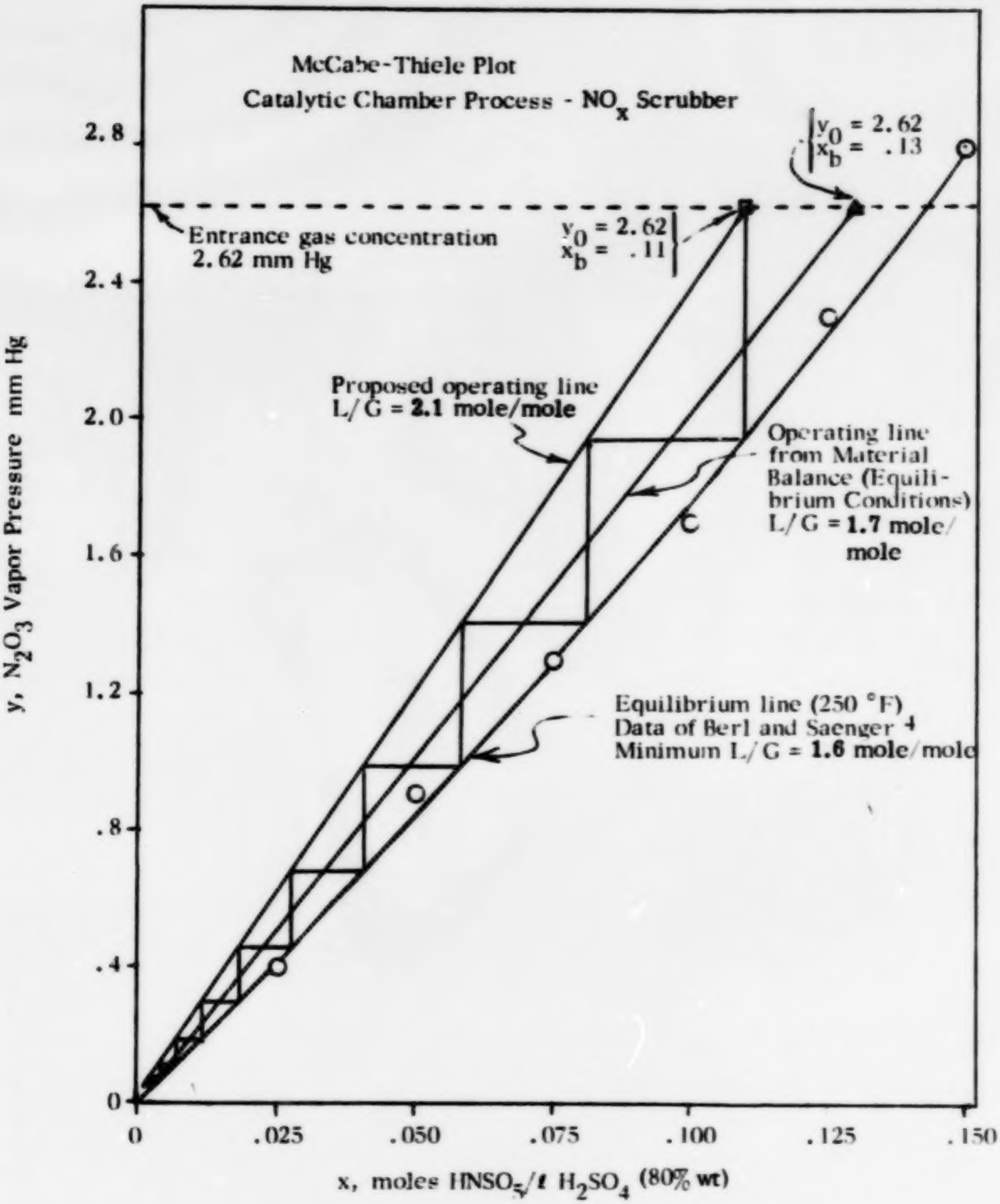


Fig. 39. McCabe-Thiele plot for NO$_x$ scrubber in Catalytic Chamber Process

An assumption is made that L and G are constant throughout the length of the column without a significant error. The material balance for the solute is:

$$L\,x_a + G\,y_b = L\,x_b + G\,y_a$$

This can be rearranged to give:

$$\frac{y_b - y_a}{x_b - x_a} = \frac{L}{G}$$

From examination of Figure 39; it is clear that L/G defines the slope of the operating line.

The equilibrium line plotted in Figure 39 is taken from the data of Berl and Saenger[4] for an operating condition of 250 °F as determined earlier. (The temperature is based on a scrubber that is treating a gas containing 6.7% excess water with 80% sulfuric acid and must therefore maintain a water vapor pressure of 51 mm Hg. The original flue gas contained 7.3% water, with the difference being used to form 80% sulfuric acid with the oxidized SO_2.)

Operating terminal conditions are based on data obtained from the material balance in Table I. The one condition that cannot be varied is the concentration of N_2O_3 in the gas entering the scrubber. From the material balance:

$$y_b = \frac{8.73\ \text{lb}\ N_2O_3}{1000\ \text{lb gas}} \Bigg| \frac{\text{mol}\ N_2O_3}{76\ \text{lb}\ N_2O_3} \Bigg| \frac{30\ \text{lb gas}}{\text{mol gas}} \Bigg| \frac{760\ \text{mm}}{}$$

$$y_b = 2.62\ \text{mm (as}\ N_2O_3\text{, or 6900 ppm}\ NO_x)$$

Again, using the material balance:

$$y_a = \frac{76\ \text{lb}\ N_2O_3}{10^6\ \text{lb gas}} \Bigg| \frac{\text{mol}\ N_2O_3}{76\ \text{lb}\ N_2O_3} \Bigg| \frac{30\ \text{lb gas}}{\text{mol gas}} \Bigg| \frac{760\ \text{mm}}{}$$

$$y_a = 0.023\ \text{mm Hg (as}\ N_2O_3\text{, or 60 ppm}\ NO_x)$$

$$x_b = \begin{array}{c|c|c|c} 8.65\ \text{lb}\ N_2O_3 & \text{mol}\ N_2O_3 & 2\ \text{mol}\ HNSO_5 & 454\ \text{g}^-\ \text{mol}\ HNSO_5 \\ \hline 3021\ \text{lb}\ H_2SO_4 & 76\ \text{lb}\ N_2O_3 & \text{mol}\ N_2O_3 & \text{lb-mol}\ HNSO_5 \end{array}$$

$$\times \begin{array}{c|c} \text{lb}\ H_2SO_4 & 1727\ \text{g}\ H_2SO_4 \\ \hline 454\ \text{g}\ H_2SO_4 & \ell\ H_2SO_4\ (80\%) \end{array}$$

$x_b = 0.13$ mol $HNSO_5/\ell$ H_2SO_4 (or 0.96% wt $HNSO_5$)

$$x_a = \begin{array}{c|c|c} 0.066\ \text{lb}\ N_2O_3 & 2 & 1727 \\ \hline 3000\ \text{lb}\ H_2SO_4 & 76 & \end{array}$$

$x_a = 0.001$ mol $HNSO_5/\ell$ H_2SO_4 (or 0.007% wt $HNSO_5$)

The terminal points for this operating line are therefore:

$x_a = 0.001$ mol $HNSO_5/\ell$ H_2SO_4	$x_b = 0.13$ mol $HNSO_5/\ell$ H_2SO_4
$y_a = 0.023$ mm Hg	$y_b = 2.62$ mm Hg

This line is also plotted on Figure 39.

Since the data shown in this operating line were obtained from equilibrium condition assumptions, one end of the line actually touches the equilibrium line. This means that it would take an infinite number of theoretical stages to perform the desired operation and it is, therefore, impossible.

Given the equation for the slope of the operating line, it is possible to obtain the L/G ratio for this operating line and the minimum L/G which is the slope of the equilibrium line. The minimum L/G is ~~2.84~~ 1.6 and the L/G for the material balance-based operating line is ~~3.05~~ 1.7, as given earlier.

In order to achieve the absorption desired in this process, it is necessary to determine more realistic terminal points. If we assume that the acid entering the column must contain some N_2O_3, then we have to increase the allowable effluent gas content of N_2O_3. At the same time, a faster separation can be achieved if the liquid flow rate is increased, thus diluting the effluent acid. The following terminal conditions were chosen for trial:

y_b = 2.62 mm Hg (6900 ppm NO_x) y_a = 0.046 mm Hg (120 ppm NO_x)

x_b = 0.11 mol $HNSO_5/\ell$ H_2SO_4 x_a = 0.001 mol $HNSO_5/\ell$ H_2SO_4

This new operating line is also plotted on Figure 39, and the usual step-wise McCabe-Thiele procedure is used to determine the theoretical number of equivalent plates. The number of plates is 10, certainly a reasonable number.

By increasing the liquid flow, the L/G ratio is increased. Using the same material balance equation as before, the L/G for the new line is 2.1 mole/mole. Obviously, by increasing this ratio (and thereby diluting the effluent acid), the value for x_b will be decreased and the number of theoretical plates will decrease. Alternatively, if more N_2O_3 is allowed to escape to the atmosphere, fewer theoretical plates are needed. The figures given here for this operating line are based on 150 ppm of N_2O_3 escaping with the stack gas which represents 25% of the NO_x which came in with the flue gas.

In order to evaluate the concept of high temperature scrubbing, a 1 1/2-in. glass column was packed with 2 ft of Berl saddles and was fed with countercurrent streams of N_2O_3 in N_2 and 80% H_2SO_4 at an L/G ratio of about 1.7 mole/mole. All entering streams and the column were heated so that the absorption would take place at about 250° F. All exit streams were analyzed for NO_x content, and a complete material balance was made. Table XXVII shows the column conditions and the concentrations of the exit and entrance streams for two runs. It is significant to note that without optimizing column height or operating conditions, recoveries in excess of 98% were achieved with very low material balance errors.*

These data are very encouraging and show that there will be no problem in scrubbing the reacted flue gas with 80% H_2SO_4 at 250 °F and removing 99% of the NO_x content. It will also be possible to reduce the exit gas concentration to about 150 ppm NO_x. Obviously, use of high temperature isothermal scrubber is a practical way of preventing the absorption of water by the scrubber acid and thus eliminate the need for the acid concentration.

4) Concentration of N_2O_3 in the Stripper

a) Gas Phase Catalytic Oxidation of NO

As mentioned above, about one-half of the heat requirement of the Modified Chamber Process can be eliminated if a technique can be found to concentrate the N_2O_3 in the stripper gas to a

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*Note: The actual recoveries were probably higher than those shown because of the difficulty in reading the NO peak in the IR spectrum used to analyze the exit gases. At the high temperature used, there is a good deal of water removed (about 50 mm Hg) and one of the water bands partially overlaps the NO band, thus making it hard to properly read the exact NO concentration. The figures reported are the worst case with a strong likelihood that more than 75% of the NO reported is really water. Adjusting the recovery for the water band shows recoveries of about 99.5% NO_2 and effluent NO_x concentrations of less than 40 ppm. For future experimentation, the NO can be recalibrated in the presence of water to eliminate any error, but for the time being these results are satisfactory.

Table XXVII. Results of High Temperature Absorption Experiments

	Run 1	Run 2
Entering acid temperature, °F	265	265
Column temperature, °F		
Top	240	255
Bottom	255	255
Entering gas temperature, °F	300	300
H_2SO_4 flow rate, cc/min	24	30
Entering gas flow rate, cc/min-STP		
N_2O_3	35	35
N_2	12000	12000
Entering N_2O_3 concentration, ppm	2900	2900
Exit acid concentration, $HNSO_5$-wt %	0.86	0.86
Exit gas concentration, ppm		
NO	<100	<65
NO_2	10	10
Total NO_x	110	75
Material balance error, %*	10	13.8
NO_x removal, %	>98	>98.7

$$\text{*Material balance error} = \frac{NO_x\text{ (in-gas)} - [NO_x\text{ (out-gas)} + NO_x\text{ (out-acid)}]}{NO_x\text{ (in-gas)}} \times 100$$

level which will allow the oxidation of the NO content of the gas in a reasonable volume without heating the nitrose. In the originally proposed chamber process, the limitation is the vapor pressure of N_2O_3 above the hot nitrose entering the stripper from the scrubber. Therefore, in order to obtain a concentration of N_2O_3 in the stripper gas that is appreciably higher than the concentration in the reacted flue gas, the nitrose has to be heated considerably.

If a high temperature stripper is operated as in Fig. 40, it is obvious that the volume of gas necessary to recover the N_2O_3 is exactly equal to the original amount of flue gas (if we assume equilibrium conditions). This is clearly impractical since the concentration of N_2O_3 would be so low as to require enormous contact time with the 2-3% oxygen present in the flue gas to effect 100% oxidation to NO_2.

The only alternative is to remove the dissolved NO_x by thermal stripping, which brings us to the problem of handling recycle water. If the stripper is operated hotter than the scrubber so as to raise the vapor pressure of N_2O_3, less gas is needed to carry off the NO_x then was present in the original flue gas. The N_2O_3 would then be more concentrated, thus speeding up the reoxidation process.

Figure 41 shows such a scheme where the scrubber is operated so that the gas exiting to the atmosphere contains as much water as enters with the reacted flue gas. At the same time, the stripper conditions are such that only 31% of the original flue gas at 1250°F is required to heat the acid to a temperature such that the concentration of the N_2O_3 in the exit gas is raised to about 1%. This amount of required heat is equivalent to burning an additional 18% coal, which might well be within the capabilities of the average power plant.

The heat requirement is so low because the acid no longer has to be heated to boiling (395°F for 80% acid). This is because reconcentration of the acid is not required since no water has been removed from the original flue gas stream. The only transfer of water in the system is

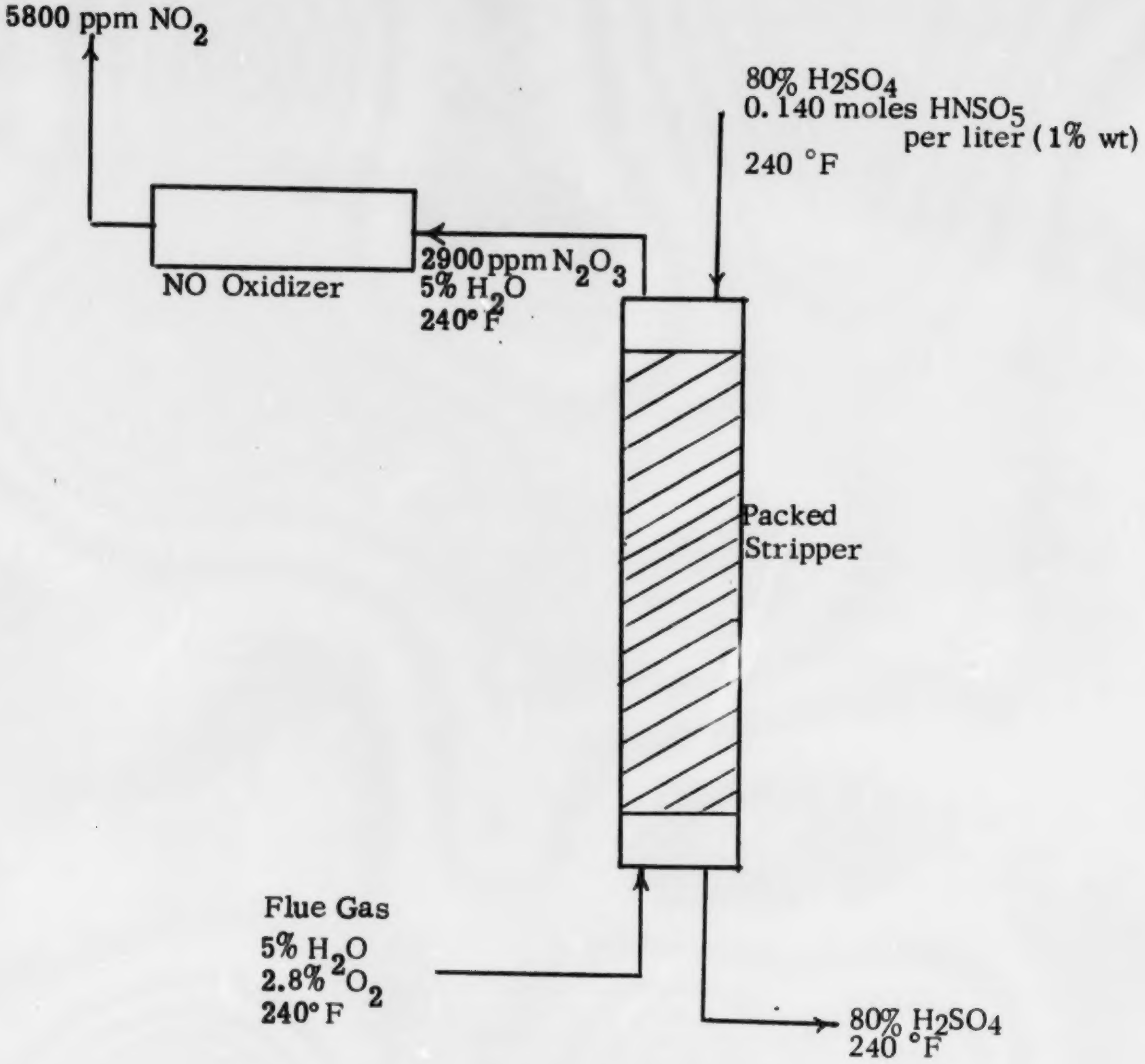
5800 ppm NO_2
80% H_2SO_4
0.140 moles $HNSO_5$ per liter (1% wt)
240 °F
NO Oxidizer
2900 ppm N_2O_3
5% H_2O
240° F
Packed Stripper
Flue Gas
5% H_2O
2.8% O_2
240° F
80% H_2SO_4
240 °F

Fig. 40. High Temperature Stripper with NO Oxidizer

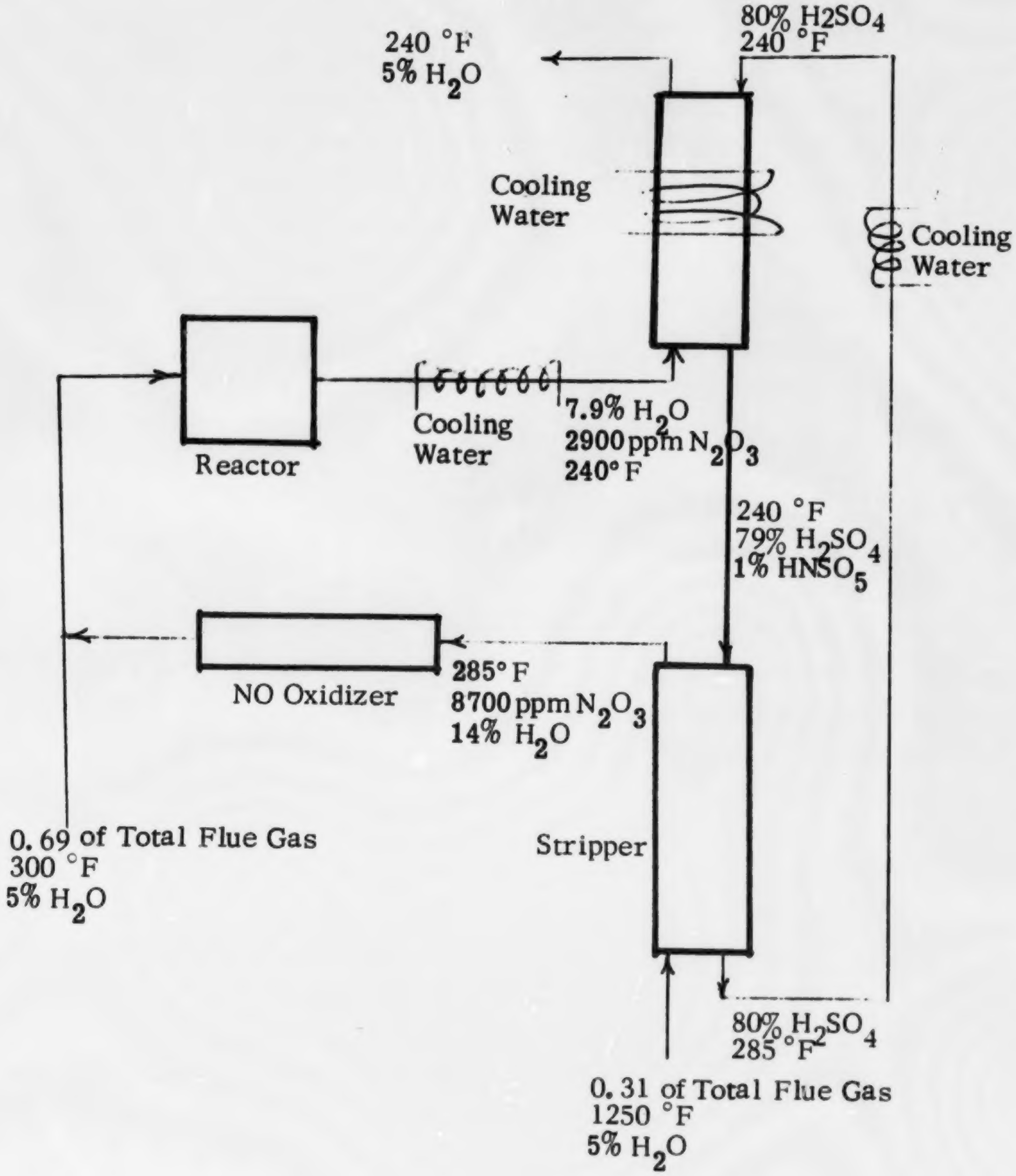
240 °F
5% H_2O
80% H_2SO_4
240 °F
Cooling Water
Cooling Water
Reactor
Cooling Water
7.9% H_2O
2900 ppm N_2O_3
240° F
240 °F
79% H_2SO_4
1% $HNSO_5$
NO Oxidizer
285° F
8700 ppm N_2O_3
14% H_2O
Stripper
0.69 of Total Flue Gas
300 °F
5% H_2O
80% H_2SO_4
285 °F
0.31 of Total Flue Gas
1250 °F
5% H_2O

Fig. 41. Modified High Temperature Process

the vaporization of water in the stripper and the reabsorption of the same amount of water in the scrubber.

One matter that must be determined is the concentration of $HNSO_5$ in the acid leaving the stripper. (Since the stripper will not operate under equilibrium conditions, it is hard to predict the actual operating conditions and $HNSO_5$ concentrations. These are probably best determined experimentally.) The amount of N_2O_3 in the recycle acid will determine the amount of NO_x lost to the atmosphere since the stack gas is in equilibrium with this acid stream. It is important to keep this to a minimum in order to take advantage of the opportunity to manufacture and sell nitric acid using the NO_x in the original flue gas as the raw material source.

In order to make this system operate properly, three heat exchangers would have to be added, as shown in Fig. 41. The flue gas will have to be cooled so that it enters the scrubber at 250 °F. rather than the 330 °F of the combined reacted flue gases. Heat will have to be removed from the scrubber in order to maintain the isothermal condition. This excess heat is developed by the absorption of N_2O_3 and the solution of water in the scrubber. The third heat exchanger is used to cool the acid leaving the stripper from 285 °F back to 250 °F for recycle. This last quantity of heat is the largest heat loss in the system and may have some value, although it is not a high quality heat source.

After leaving the stripper the gas contains N_2O_3 which must be oxidized to NO_2 before it is mixed with the remaining flue gas and fed to the reactor. The reaction between NO and O_2 occurs faster at lower temperatures which would require the gas to be cooled at this point. However, even if the gas were to be cooled, the contact time required for the uncatalyzed reaction would be quite long, assuming that the flue gas contains 2.8% oxygen. Table XXVIII shows the contact times necessary to achieve 80 or 90% reaction with this level of oxygen with and without a charcoal catalyst. The data are plotted in Fig. 42.

Table XXVIII. Contact Time for Oxidation of Nitric Oxide (2.8% O_2)

NO Concentration (%)	Degree of Reaction (%)	Reaction Time (sec) Carbon Catalyzed	Uncatalyzed
0.3	90	22.3	4667
0.3	80	9.9	2062
1.0	90	7.5	1550
1.0	80	3.2	668
5.0	90	2.5	525
5.0	80	1.4	284

The data in this table are based on the reaction rate equation developed by Burdick and given in Section V-E.

Burdick found that below 50 °C, k had a value of about 12 and dropped as the temperature of the uncatalyzed reaction was increased. He found the same temperature effect with catalyzed reactions of dry gases, while the rate constant rose to about 10,000. If moist gases were used, the value of k dropped to about 1000 but now increased as the temperature increased. He accounted for this by assuming that the moisture in the gas tended to adsorb on the charcoal, using up active catalytic sites, but heating desorbed the water, thus increasing the activity of the catalyst.

Thus, it appears to be advantageous to catalytically oxidize the NO at as high a temperature as possible. The gas would not have to be cooled and relatively low concentrations of NO could be tolerated (~1%). Examination of Table XXVIII and Fig. 42 reveals that very fast reaction times can be achieved with 2.8% oxygen and NO concentrations above 1%. The catalyst so markedly increases the reaction rate that consideration might be given to using all the flue gas in the stripper at low temperature and thus avoid the water recycle and the sensible heat loss incurred by the thermal cycling of the acid.

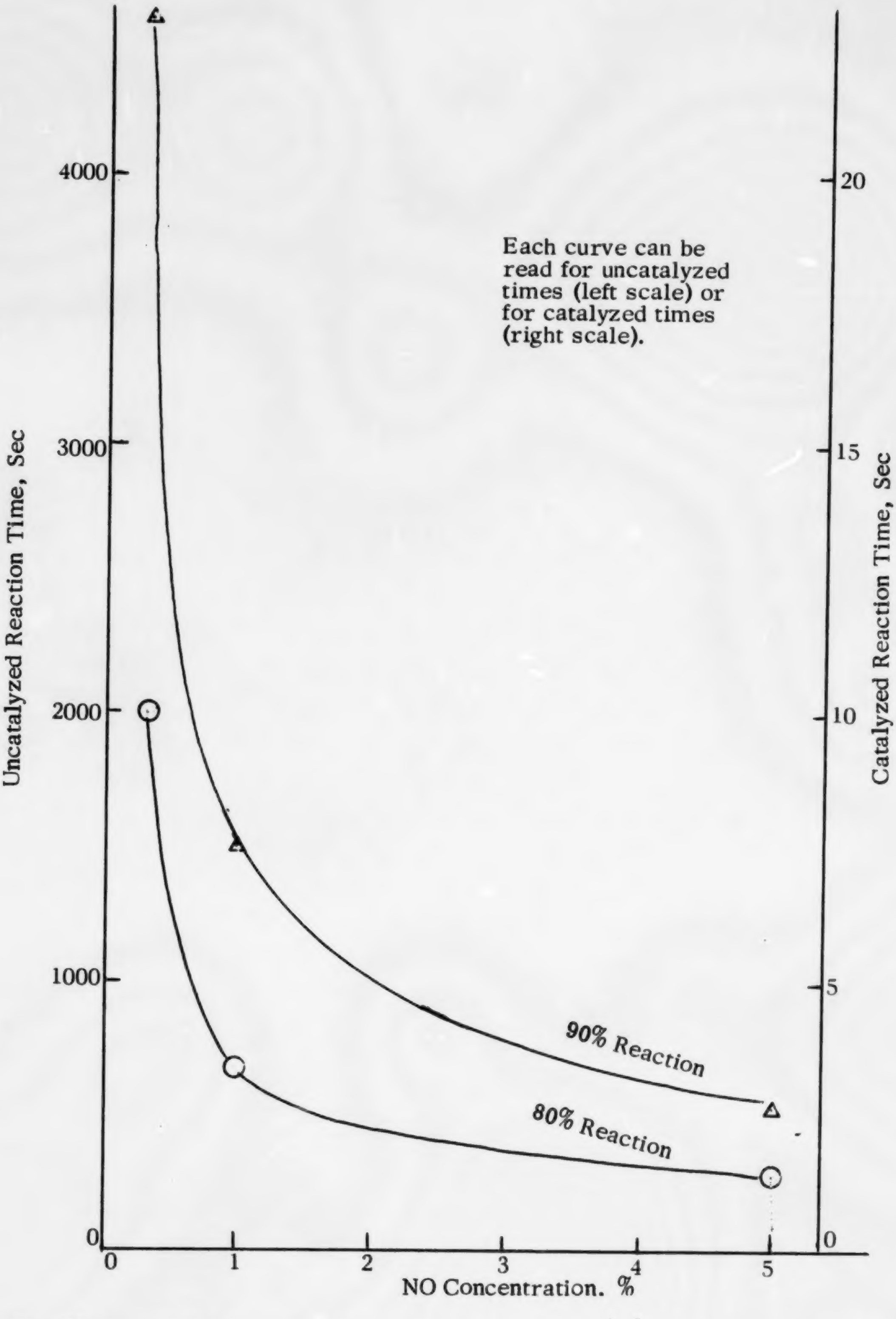

Fig. 42. NO Oxidation Times for Charcoal Catalyzed and Uncatalyzed Reactions (2.8% O_2, 25-50°C) to Achieve 80% and 90% Yields From the Reaction: $NO + 1/2\ O_2 \rightarrow NO_2$

Use of this catalytic NO oxidation technique with the process shown in Fig. 41 would require the use of 18% additional coal to provide the heat needed to concentrate the N_2O_3 to about 1%. This would permit 90% oxidation in 7.5 seconds (or 80% oxidation in 3.2 sec), thus reducing the size of the required oxidation chamber to a more reasonable volume. In a system designed for an 800 megawatt power plant (7.25 million lb/hr of flue gas) this would mean using an oxidizing chamber 25 ft in diameter and about 50 ft high to achieve 80% oxidation.

These schemes depend on maintaining the proper balance of NO_2 and NO in the various stages of the system. If the NO oxidizer were set up to convert only 80% of the NO to NO_2, then additional NO_2 must be kept in the system so that after the reaction with SO_2 the NO_2 to NO ratio would be 1/1. This would also change the concentration of $HNSO_5$ in the scrubber effluent acid and would affect the operation of the stripper.

b) Liquid Phase Reduction of $HNSO_5$

Although the catalytic oxidation of NO as described in the previous section has a great deal of merit and does result in the reduction of the extra process heat needed, it still requires 18% additional fuel. If the catalytic oxidation of NO could be accomplished after a stripping operation that did not require this additional fuel, a further saving could be realized.

Basically, what must be done is to reduce the solubility of the oxides of nitrogen in the sulfuric acid. As was discussed in an earlier section, NO and NO_2 alone are relatively insoluble in sulfuric acid, but in equimolar quantities they are very soluble. Since the gases are absorbed in the scrubber in equimolar quantities they will be present in the nitrose in that mole ratio. In order to accelerate their removal from solution it would be necessary to unbalance the mole ratio, either by oxidizing the NO to NO_2 or reducing the NO_2 to NO.

A method was suggested for the liquid phase reduction of N_2O_3 to NO and thus speed up the vaporization of the oxides. In choosing the technique we kept in mind that it was important to avoid using a reagent that would leave an unwanted component in the acid after the denitration was accomplished. The choice for the reducing agent was ammonium sulfate, assuming the following reaction:

$$10\ HNSO_5 + (NH_4)_2\ SO_4 + 2\ H_2O = 12\ NO + 11\ H_2SO_4$$

The experiments consisted of a flask containing the $HNSO_5$ and $(NH_4)_2SO_4$ solution. The air above the solution was purged with nitrogen to avoid oxidation of any resultant NO before it could be analyzed. The analysis was performed with the Perkin-Elmer one-meter folded-path gas cell in the Model 457 infrared spectrophotometer.

No visible reaction occurred at room temperature, but a vigorous bubbling was observed above 60 °C with the effluent gas being only slightly brown in color. Analysis of this gas showed very low concentrations of NO and NO_2, considerably lower than their equilibrium vapor pressures at this temperature. The experiment was rerun using CO_2 as the inert gas in order to determine whether or not the reduction had gone all the way to nitrogen. The effluent gas was virtually colorless. The analysis showed no oxides of nitrogen and about 5 mm Hg of CO_2, indicating that all the N_2O_3 in solution had indeed been reduced to nitrogen (which cannot be analyzed by infrared techniques). Analysis of the remaining solution revealed almost complete removal of the $HNSO_5$. An experiment was run where an attempt was made to catalyze the reaction with charcoal at lower temperatures, but the results were not encouraging. The concept still appears interesting, but work was discontinued until a better reducing agent could be found.

c) Liquid Phase Catalytic Oxidation of $HNSO_5$

A clue to a possible answer to the problem was obtained by examining the reactions occurring during the nitrogen oxide recovery and reoxidation:

$$2\ HNSO_5 + H_2O \xrightarrow[\Delta]{} N_2O_3 + 2\ H_2SO_4$$

$$N_2O_3 \rightarrow NO + NO_2$$

$$\underline{NO + \tfrac{1}{2}\ O_2 \rightarrow NO_2}$$

$$2\ HNSO_5 + H_2O + \tfrac{1}{2}\ O_2 \rightarrow 2\ NO_2 + 2\ H_2SO_4$$

The net reaction equation suggests that the process is in effect, the oxidation of nitrosylsulfuric acid, implying that if a way could be found to oxidize the $HNSO_5$ in the liquid phase, the process might be accelerated.

This idea was evaluated experimentally by passing a nitrose solution countercurrent to air in a packed column and measuring the N_2O_3 concentration of the effluent gas. As might be expected from equilibrium considerations, the N_2O_3 content of the gas was very low. In order to accelerate the oxidation of the nitrose it was decided to push the reaction by packing the column with some material that might reasonably be expected to act as a catalyst. Activated charcoal was decided on because it was known to catalyze the air oxidation of nitric oxide. The previous experiment was rerun using an activated charcoal packing in the column with the visual result that the acid foamed when it contacted the charcoal giving off brown fumes which were apparently NO_2. Analysis of the effluent gas stream showed an enormous increase in the NO_2 content, well in excess of the equilibrium vapor pressure above the nitrose under these conditions. The results are shown in Table XXIX.

Clearly, the presence of charcoal had a startling effect on the solubility of the nitrogen oxides in sulfuric acid. Analysis of the effluent acid showed that effectively all the nitrogen oxide content of the nitrose had been removed and transferred to the gas stream without the limitation of equilibrium vapor pressures to restrict the oxide concentration of the gas.

Table XXIX. Results of Catalytic $HNSO_5$ Oxidation Experiments*

Carrier Gas	Packing	Exit Gas Concentration (mm Hg)† NO	Exit Gas Concentration (mm Hg)† NO_2
N_2	Saddles	<0.01	<0.01
Air	Saddles	<0.01	0.024
Air	Charcoal	<0.01	0.75

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* Test conditions: Temperature = 25 °C
Acid flow rate = 10 cc/min
Acid concentration = 0.7% $HNSO_5$ in 80% H_2SO_4
Gas flow = 0.25 SCFM.
Packing height = 20"
Column diameter = 1.5"

† All concentrations were taken 5 minutes after the gas started to pass through the liquid and packing. Equilibrium vapor press of N_2O_3 under these conditions is 0.15 mm Hg. Exit acid showed no residual NO_x content.

Although all the NO_x content of the acid had been removed (as determined by analysis of the effluent acid), a material balance around the column disclosed that only one-third of the NO_x that had apparently been fed to the column had been recovered as NO_2 in the effluent gas. There are two contributing factors to this anomaly: (1) experimental error in measuring acid flows and gas concentrations, and (2) the partial reduction of the NO_2 to N_2O. The largest source of NO_2 disappearance was undoubtedly the formation of N_2O which was not measured during these experiments, but was detected in subsequent experimentation. This problem is discussed below. The important conclusion to be derived from these tests is that this treatment completely removed the NO_x content of the sulfuric acid.

This experimentation was the basis for the catalytic stripper discussed in some detail in Section IV-F. This breakthrough makes possible the reoxidation of the oxides of nitrogen without the additional heat requirement of the Modified Chamber Process, thereby saving a considerable heat expense.

One problem that has appeared in these experiments was that the NO_2 seemed to be reacting with the carbon forming CO_2 and N_2O, which caused the charcoal bed to break up and form fines which plugged the column. A series of experiments were performed to try to determine the cause of these changes and ways to avoid them.

(1) Degassing the charcoal. On the suggestion of applications chemists at Witco Chemical Co. who have an extensive background in uses of activated carbon, we attempted to slow down the oxidation of the carbon by removing the adsorbed oxygen from the surface of the carbon particles. Although it is known that the adsorbed oxygen plays a significant role in the catalytic behavior of the carbon, it was felt that there was excess activity available on the carbon and some could be sacrificed in order to increase stability.

Samples of activated carbon were kept in boiling water for prolonged periods of time to degas the particles before using them to pack a column. The column passed water very easily, but when the air was passed countercurrent to 0.7% $HNSO_5$ solution in 80% H_2SO_4, the effluent acid rapidly became discolored with finely divided carbon particles and the column soon plugged up and no liquid could pass, although the air was able to go through the bed. It was apparent, from the evolution of brown fumes from the top of the column, that $HNSO_5$ was being oxidized to NO_2. The gas analysis showed the presence of NO_2, N_2O, and CO_2, although quantitative measurements were not possible. Other experiments were made with this column using concurrent flow of gas and liquid, but there was only slight improvement. It was obvious that the degassing did not prevent the breakdown of the carbon.

(2) Other forms of carbon. Again working on the hypothesis that some of the catalytic sites on the carbon were too active and were causing the oxidation and breakdown of the particles, we tried using coal (both hard and soft types) and coke to catalyze the reaction. Batch experiments at room temperature showed no reaction occurring and the experiments were discontinued.

(3) Silica gel. Batch tests were run with particles of silica gel used to attempt the catalytic oxidation of the $HNSO_5$. Using 80% H_2SO_4 solutions of the nitrose, it was found that no NO_2 was evolved even at temperatures above 200°F. In addition, the gel particles appeared to be absorbing water and shattering in the process. It is possible that the active sites on the silica gel were involved in absorbing water and were not available for $HNSO_5$ oxidation, but the fact that this process will probably not be feasible for acid concentrations above 92% tends to mitigate against further experimentation with silica gel.

(4) Water glass treatment. There is evidence in the literature that the oxidation of activated carbon can be inhibited by coating the carbon particles with a layer of silica formed by precipitation from water glass solutions. The carbon is first washed with a dilute (5%) solution of

sodium silicate and then washed with a 20% HCl solution to precipitate the silica.

This treatment was performed on a batch of activated carbon from Witco (type 256, particle size 4×10 mesh which was then packed in a column. Countercurrent contact of a nitrose solution with air produced NO_2 in the gas stream but also produced an effluent acid stream that was discolored although considerably lighter than that with untreated carbon.

A second batch of the same carbon was treated three times with the water glass and another column was prepared. A number of experiments were performed with this column; the results and experimental conditions are shown in Table XXX.

It is significant that the water glass treatment did prevent the oxidation of the carbon while maintaining the catalytic activity of the activated charcoal, and that the remedial effect was only temporary, with catalyst oxidation and particle breakdown occurring after several hours of operation. The overall results suggest that the washing with 80% H_2SO_4 has removed the protective silica coating, implying that it would be worthwhile to try to find a coating material that is not soluble in 80 to 92% H_2SO_4.

An unexpected result was the heating of the column. As shown in the table, the column temperature rose as soon as the acid contacted the charcoal. Prior to the first run, the acid was passed through the column causing a temperature rise from 70 to 160 °F. When nitrogen was passed through the column bed, the temperature dropped to 135°F and remained at this steady state value throughout the first four experiments, which took about 4 1/2 hr of continuous running to complete.

It is also surprising that the oxidation of the N_2O_3 took place in the first four experiments without the presence of oxygen. It would seem that some reaction took place between the nitrose and the charcoal, but it is not clear what was happening. For the N_2O_3 to be oxidized, another

Table XXX. Results of Catalytic Oxidation of $HNSO_5$ Using Water-Glass Treated Charcoal

Experiment No.	Carrier Gas	Column Temperature, °F*	Effluent Gas Composition, mm Hg				N_2O_3 Removed %+	Material Balance Error, %‡
			NO	NO_2	N_2O	CO_2		
1	N_2	135	1.8	1.9	<0.01	0	—	—
2	N_2	135	12.0	0.65	<0.01	0	—	—
3	N_2	135	2.9	0.30	<0.01	0	85	-20
4	N_2	135	4.1	1.7	<0.01	0	88	+22
5	Air	95	0.03	1.9	<0.01	0	78	-4
6	Air	85	<0.01	0.30	<0.01	0.08	45	-34
7	Air	80	<0.01	0.17	<0.01	0.20	37	-31
8	Air	105	<0.01	1.95	<0.01	1.05	88	-53

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*Steady state temperature.

+Based on analysis of the effluent acid.

‡Minus error indicates less N_2O_3 recovered than was put in the column:

$$\text{Material balance error} = \frac{NO_x\ (\text{in}) - NO_x\ (\text{out})}{NO_x\ (\text{in})} \times 100$$

material had to be reduced, and there is no evidence that this occurred (very little N_2O was formed and the material balance deviation was relatively small).

The next three experiments (performed after the column had been washed with water for 30 min and allowed to sit wet (overnight) show a sharp decrease in the amount of NO being formed (which is expected, since the oxygen present would oxidize the NO to NO_2) and an erratic quantity of NO_2 in the exit gas. At the same time, the amount of CO_2 increased, suggesting that the silica was wearing off, allowing the carbon to be oxidized. At this time, the effluent acid started becoming black with suspended carbon fines. However, it is hard to understand why the NO and NO_2 production decreased when the silica started to wear off. It might be said that the newly formed NO_2 was reacting with the charcoal and was reduced, but then there would have been more N_2O present in the exit gas (and the IR analysis spectrum showed no sign of a reduced species).

It is clear that a good deal more work is needed to understand the behavior of the silica treated charcoal. A decision will have to be made as to whether it is worthwhile to continue to work with the charcoal or to devote our experimental effort toward finding other suitable catalysts.

(5) Results of Process Modification Efforts. The goal in this work was the elimination of the additional heat requirements demanded by the Modified Chamber Process. The resulting process, dubbed the Catalytic Chamber Process as described in Section IV, accomplishes this goal to the extent that the process is now slightly exothermic. Additional work is required to determine operating conditions, catalyst systems and general engineering data, but the concept appears soundly supported by reliable data and gives promise of being a workable solution to the power plant flue gas pollution problem.

APPENDIX 1. Ultraviolet Spectrophotometric Analytical Techniques

Sulfur dioxide and nitrogen dioxide were analyzed in dilute gas mixtures using a modified Spex Model 1700 single beam infrared spectrophotometer and an external hydrogen arc light source. The sample was placed in an optical cell (with quartz windows), similar to the one in Fig. 43 and positioned in the light beam between the source and the entrance slit of the photometer. Changes in transmission due to absorption by the gases in the sample cell were monitored on a strip chart recorder. The full scale recorder response time was about 5 seconds.

Figure 44 shows the ultraviolet absorption of SO_2 as a function of partial pressure as determined experimentally by Tyco. The reproducibility of the data at 2860 Å was quite good in the 0.1 - 1% range. Similar data for NO_2 absorption at 5100 Å are shown graphically in Fig. 45. Again the reproducibility of measurement was good, and the sensitivity more than adequate in the concentration range of 1 - 10 volume %.

Since NO_2 absorbs to a limited extent at 2860 Å, it is necessary to introduce a small correction factor to account for the influence of NO_2 on the SO_2 absorption. (Experimental measurements showed that this SO_2 - NO_2 interaction is a minimum at 2860 Å. Hence, this wavelength was selected for SO_2 determinations as the best compromise between sensitivity, which is highest at 3082 Å, and NO_2 interference, which is least at about 2700 Å.) Since neither SO_2 nor NO absorb in the visible region of the spectrum, there is no corresponding interference by these gases with the NO_2 concentration measurements at 5100 Å.

A procedure was devised to correct the SO_2 concentration measurements for the NO_2 present. The NO_2 concentration was first measured at 5100 Å; then the 2860 Å contribution of this known concentration of NO_2 was deducted from the total absorption obtained at 2860 Å. The

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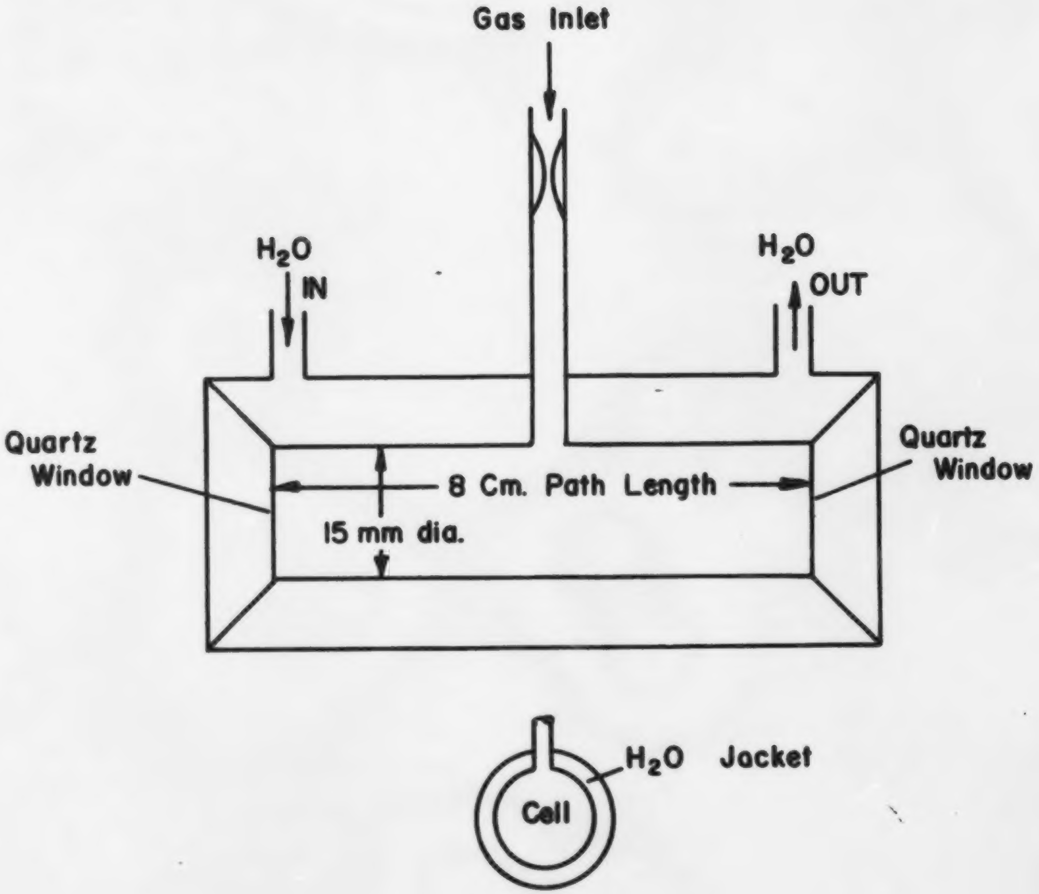
Gas Inlet
H_2O IN
H_2O OUT
Quartz Window
8 Cm. Path Length
15 mm dia.
Quartz Window
H_2O Jacket
Cell

Fig. 48. Water-jacketed UV absorption cell (15 ml volume).

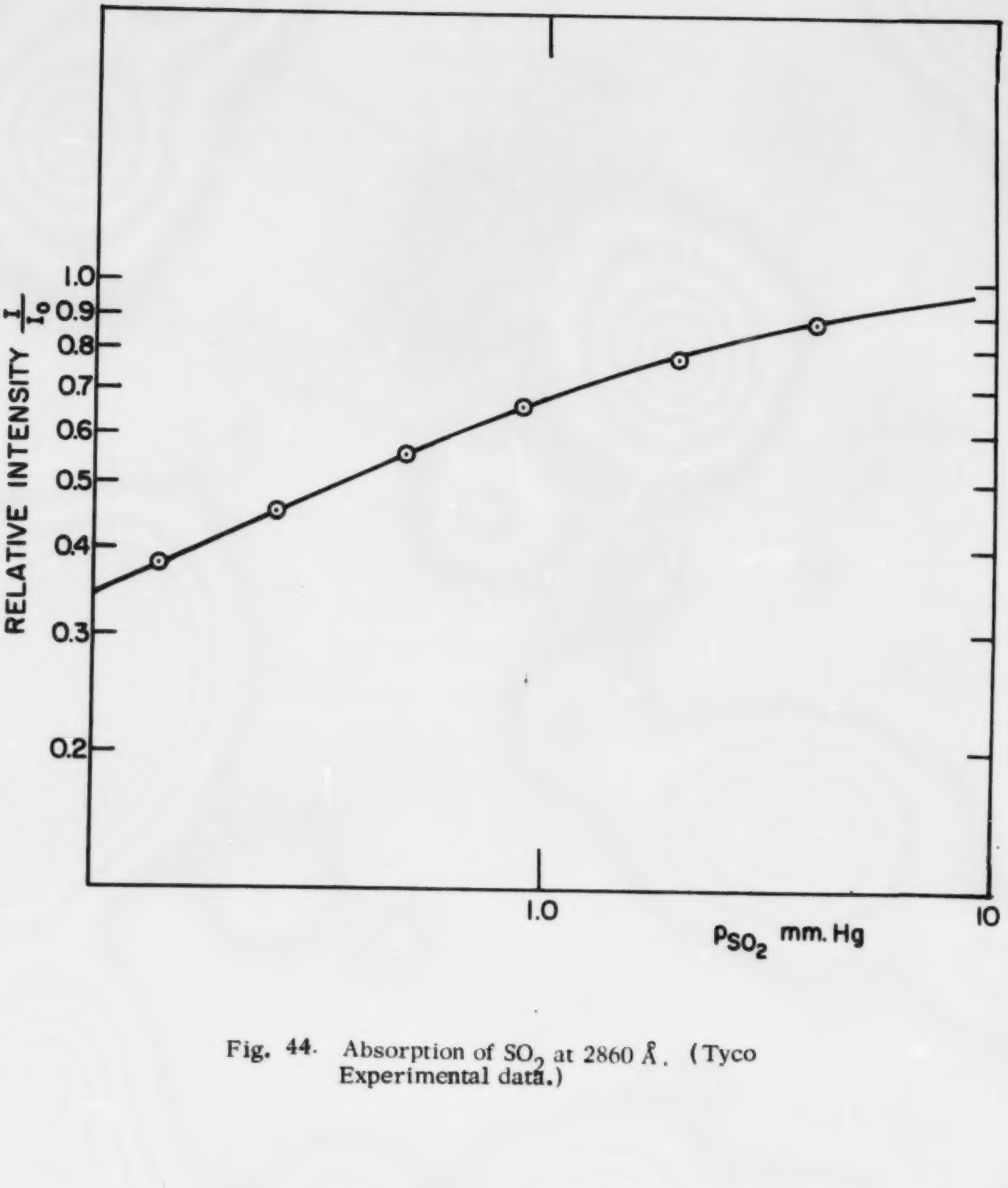

Fig. 44. Absorption of SO_2 at 2860 Å. (Tyco Experimental data.)

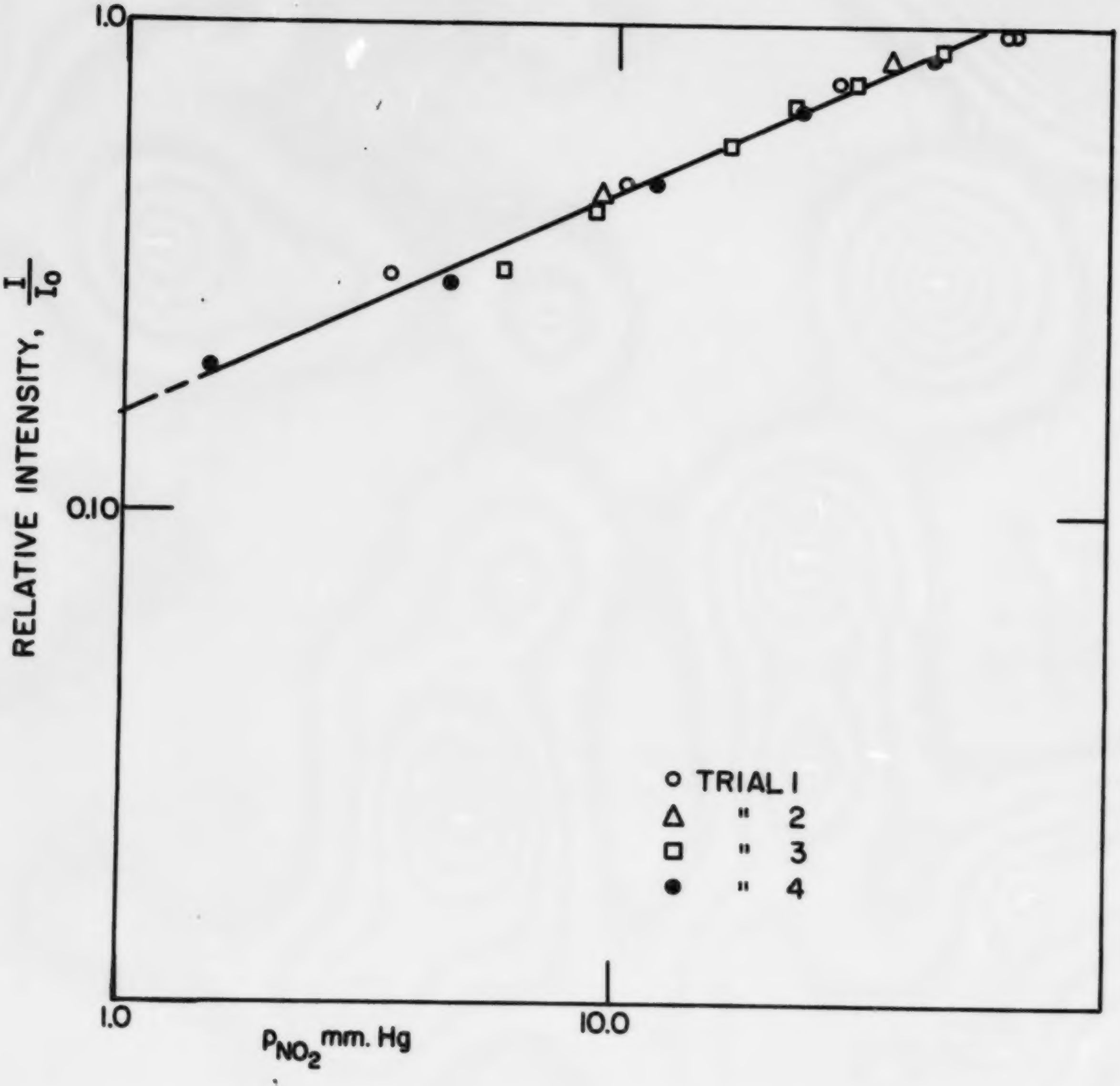

Fig. 45. Absorption of NO_2 at 5100 Å. (Tyco experimental data.)

balance was assessed due to SO_2. The accuracy of this procedure is verified by the observation that, using a linear plotting method, extrapolation of the reaction rate data to zero time yields a value for initial SO_2 concentration that corresponds closely to its actual level.

A major drawback to the UV method is its inability to detect nitric oxide in the concentration range of interest. As a result many of the gas mixtures analyzed during the experimental work have been incompletely evaluated, making it impossible to do complete material balances. As a result, although the UV method is quick and dependable, a new method had to be developed which would permit the analysis of all gaseous species in multicomponent mixtures. The infrared detection method that was adopted is presented in Appendix 2 along with wet chemical methods for absolute quantitative measurements.

APPENDIX 2. Analytical Techniques

A. Introduction

Experimental work performed during the early part of the contract clearly pointed out the need for accurate, reproducible techniques for analyzing all of the various process streams in our pilot plant system. Without this capability for complete analysis, material and heat balances cannot be worked out, making it difficult to justify conclusions based on incomplete data. Work has been completed on a series of analytical procedures which will make possible the complete analysis of all process streams. The following discussion describes the spectroscopic and classical wet chemical techniques that are used to analyze the various system streams and some of the work that has been done to further develop these methods. A list of relevant band frequencies for the spectroscopic determinations is given in Table XXXI. All possible gas phase components (NO , NO_2 , SO_2 , CO , CO_2 and N_2O) are determined by the infrared method.

B. General Gas Handling Methods

The flow rates of all gases used were measured with Brook Instrument Nos. 601, 602 and 604 flowmeters which were calibrated against a standard bubble flowmeter for each of the gases in question. This technique was followed for each of the gases used except NO_2 which required, due to its reactivity and physical properties, the use of special analytical techniques for flowmeter calibrations. A discussion of these techniques will be given in the section discussing nitrogen dioxide.

The general calibration procedure employed for each of the gases consisted of mixing measured streams of the desired gas and nitrogen and passing this mixture through the optical cell.

The spectroscopic work was accomplished through the use of a one meter folded path Perkin-Elmer gas cell with sodium chloride windows and a Perkin-Elmer double beam infrared spectrophotometer (Model No. 457). As the flow rates of each of the components was known, the partial pressure of the gas could then be calculated. Then by obtaining a log-log plot of partial pressure vs. relative intensity for a particular band, a calibration curve was made for each of the desired gases.

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TABLE XXXI. Infrared Spectral Band Frequencies for Several Gases Of Interest

Gas	Band Frequencies (cm^{-1})
NO	1900 *
NO_2	2950 *, 1750, 1600, 1260, 750
SO_2	2500, 1360, 1150 *
N_2O	3490, 2800, 2570, 2470, 2440, 2230 *, 2210, 1300, 1270
CO	2160 *, 2110
CO_2	3640 *, 2260, 700

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* Denotes band most useful for quantitative analysis work.

C. Nitrogen Dioxide

Two methods, one chemical and one spectroscopic, have been used to analyze NO_2 in the gas phase. The chemical technique involved absorption of the NO_2 in 3% hydrogen peroxide, followed by titration of the resultant HNO_3 with standard NaOH in the presence of methyl red. This method is only specific for NO_2 if there are no acidic species present in the gas, thus making it unusable for analysis of the effluent scrubber gas which may contain sulfuric acid mist, NO and SO_2. The major utility of this method is for the analysis of pure gas streams, for instance, in the calibration of flowmeters and infrared spectra.

Since this is an absolute method, a few precautions must be taken to insure accuracy. At least two absorbers must be used in series to make sure that all the NO_2 that enters the system is absorbed for analysis. In addition, care must be taken to avoid a significant amount of void gas volume in the tubing leading to the absorbers. This can be eliminated by using capillary tubing and passing through a volume of gas several hundred times the void volume of the tubing. Data obtained in the laboratory indicates an accuracy of ± 3% in the calibration of flowmeters.

In the handling of NO_2 in the laboratory some unusual procedures had to be followed: As the gas condenses at 21 °C at atmospheric pressure, the portion of the calibrating system through which pure undiluted NO_2 was passing had to be kept in a constant temperature box to avoid condensation problems. The temperature of this box, during all calibrations and operations was maintained at 35 °C.

In order to use the infrared analysis method, a series of calibration spectra were obtained using known concentrations of NO_2 (using a flowmeter calibrated with the above chemical method). The resulting relative intensity vs. concentration curve was then used to evaluate unknown gases. The bands of interest were 2950, 1750, 1600, and 750 cm^{-1}, with the 2950 cm^{-1} band appearing to be the most useful. Figure 46 shows a typical calibration curve for 2950 cm^{-1}.

Some problems have arisen through the use of the cell which require careful analysis of the spectral data obtained with it. First of all, the window material appears to be reacting with the NO_2 to form a permanent layer of sodium nitrite. This does not appreciably affect the trans-

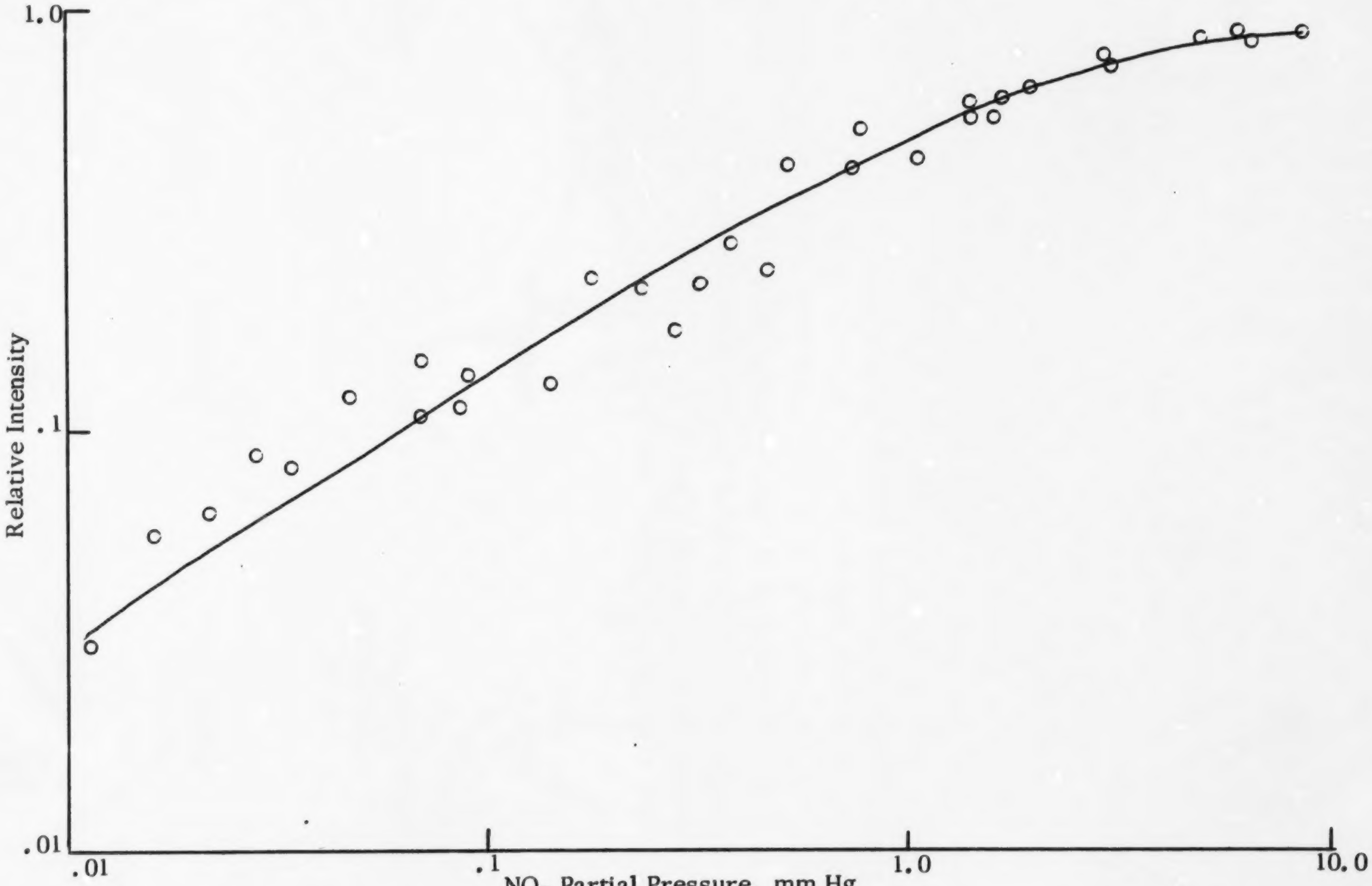

Fig. 46. Nitrogen Dioxide Calibration Curve 2950 cm^{-1}.

parency of the window, although it does create a sharp peak at 1355 cm^{-1} which has some influence on the 1260 cm^{-1} NO_2 peak.

Another more significant problem is the apparent decrease in NO_2 concentration with time when the gas sample is left in the cell and spectra taken over an extended period of time. As the NO_2 decreases, three new peaks appear at 880, 1330 and 3550 cm^{-1} which suggest the presence of organic nitrates or nitrites. These may result from the reaction of NO_2 with adhesives or seals in the cell. This phenomenon indicates that the spectrum must be obtained as quickly as possible to avoid the effect of this reaction. Data obtained over a long period of time indicate that errors in concentration will be less than a few percent if the spectrum is taken within 20 minutes, a condition well within the capabilities of the equipment.

This work has demonstrated that the NO_2 can be analyzed in the 100 - 10,000 ppm range with an accuracy of 10% if the proper precautions are taken. The sodium nitrite peak has been shown to have no effect on the analysis, and the time dependent NO_2 concentration drop can be neglected if the sample is analyzed fast enough.

D. Sulfur Dioxide

Gas phase SO_2 can be analyzed by spectroscopic means similar to the technique used above for NO_2. The peaks of interest are at 2500, 1360 and 1150 cm^{-1}, with the 1150 cm^{-1} band appearing to be the best. (This "best" peak has been chosen for all gases on the basis of reproducibility and usable concentration range.) No problems have been encountered with this gas and reproducible results in the 100 - 10,000 ppm range have been obtained with an experimental error under 10%. Figure 47 shows a calibration curve for SO_2 at 1150 cm^{-1}.

E. Nitric Oxide

NO can be analyzed in gas streams using the same spectroscopic technique as described above, with the high frequency peak of the NO doublet band at 1900 cm^{-1} being utilized. (See Fig. 48 for calibration curve.) Care must be taken in analyzing gas mixtures containing NO and oxygen since the NO slowly oxidizes to NO_2. Since the NO oxidation is very slow at low concentrations it is possible to obtain very good data by measuring the spectral

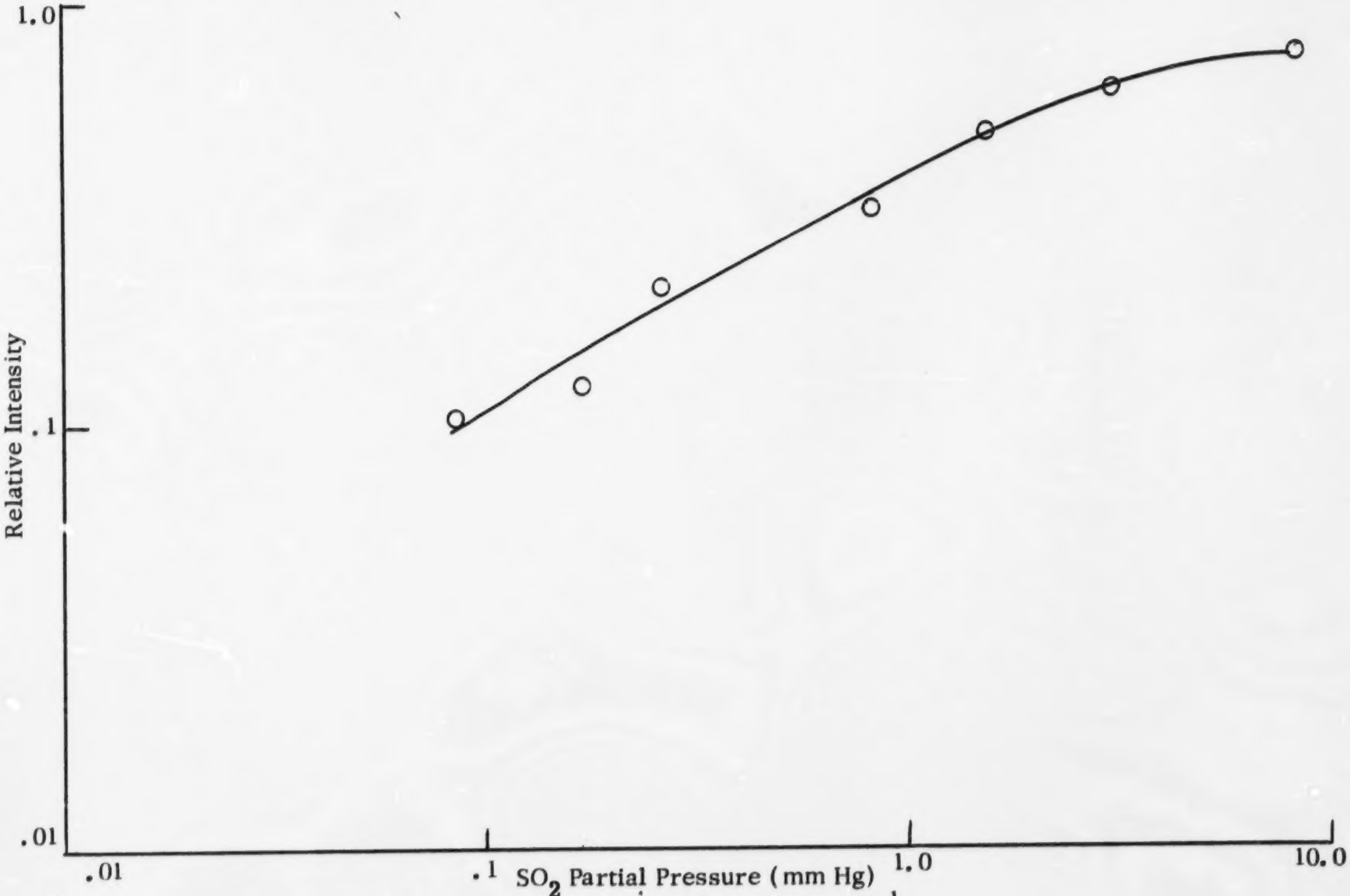

Fig. 47. Sulfur Dioxide Calibration Curve 1150 cm^{-1}.

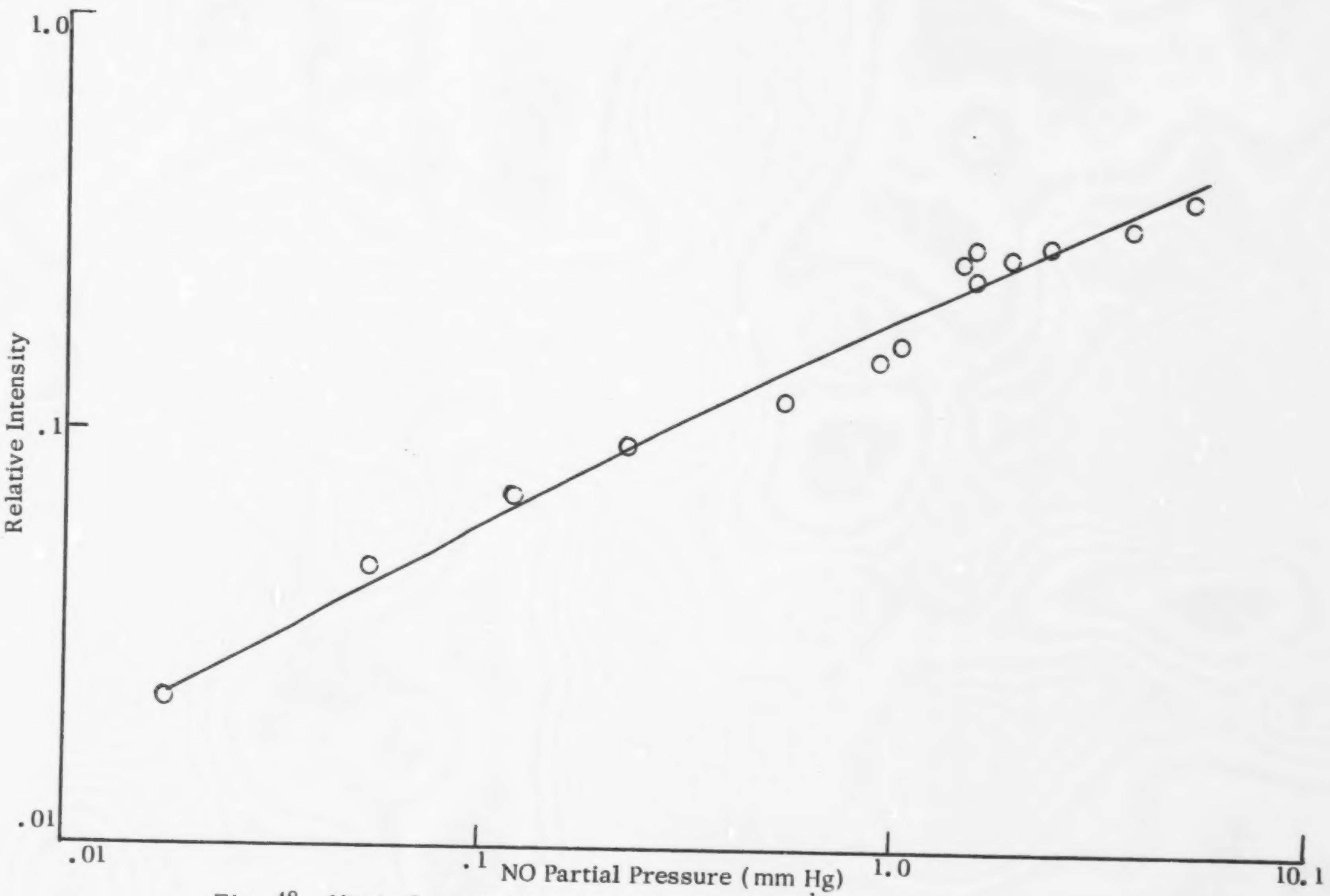

Fig. 48. Nitric Oxide Calibration Curve 1900 cm^{-1}.

intensity drop over a period of time and extrapolating back to zero time for original concentration. Experimentally it was determined that at the low NO concentration levels expected in the operation of the pilot plant it would be possible to ignore this oxidation if the oxygen content were very low and the sample evaluated immediately. Errors of less than 10% would result if care were taken in analyzing the sample.

F. Nitrous Oxide (N_2O)

In a few instances N_2O has been found in trace quantities as an unwanted reduction product. Gas phase N_2O can be determined spectroscopically by the same techniques used for NO and SO_2. The observed peaks in its spectrum are at 3490 cm^{-1}, 2800 cm^{-1}, 2570 cm^{-1}, 2440 cm^{-1}, 2210 cm^{-1}, 2230 cm^{-1}, 1300 cm^{-1}, and 1270 cm^{-1}, with the 2230 cm^{-1} band appearing to be the most usable. (The other bands disappear too rapidly with decreasing partial pressure to be of use.) No problems have been obtained in the 100 — 10,000 ppm range. Figure 49 shows a calibration curve for 2230 cm^{-1}. The flatness of this curve makes it difficult to use above .01 mm Hg, but it has been of value to determine qualitative N_2O levels.

G. Carbon Monoxide

Carbon monoxide may appear as an unwanted product from reactions between nitrogen oxides and he charcoal catalyst used in the modified stripper. Gas phase CO can be determined spectroscopically by the same methods used for the other gases. The observed peaks for this material occur at 2160 and 2110 cm^{-1}. The 2160 cm^{-1} peak is the most intense and has been used for calibration purposes. Results are shown in Fig. 50.

H. Carbon Dioxide

Gas phase concentrations of carbon dioxide can be determined by the infrared method. The principal bands occur at 3640, 2260 and 700 cm^{-1}. Of these, the 3640 cm^{-1} band appears the most satisfactory for use in calibrations. Figure 51 shows the calibration curve for this band.

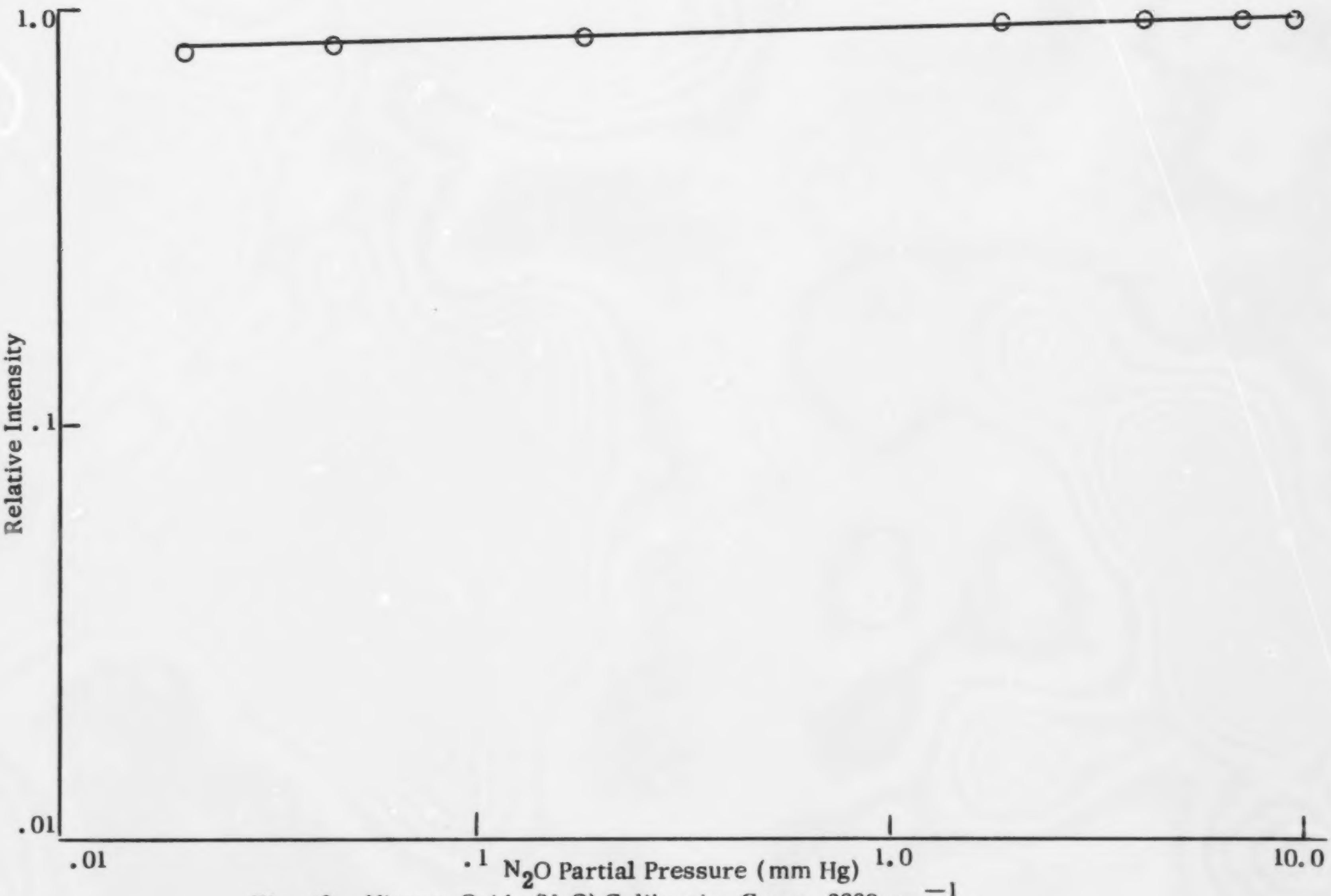

Fig. 49. Nitrous Oxide (N_2O) Calibration Curve 2230 cm^{-1}.

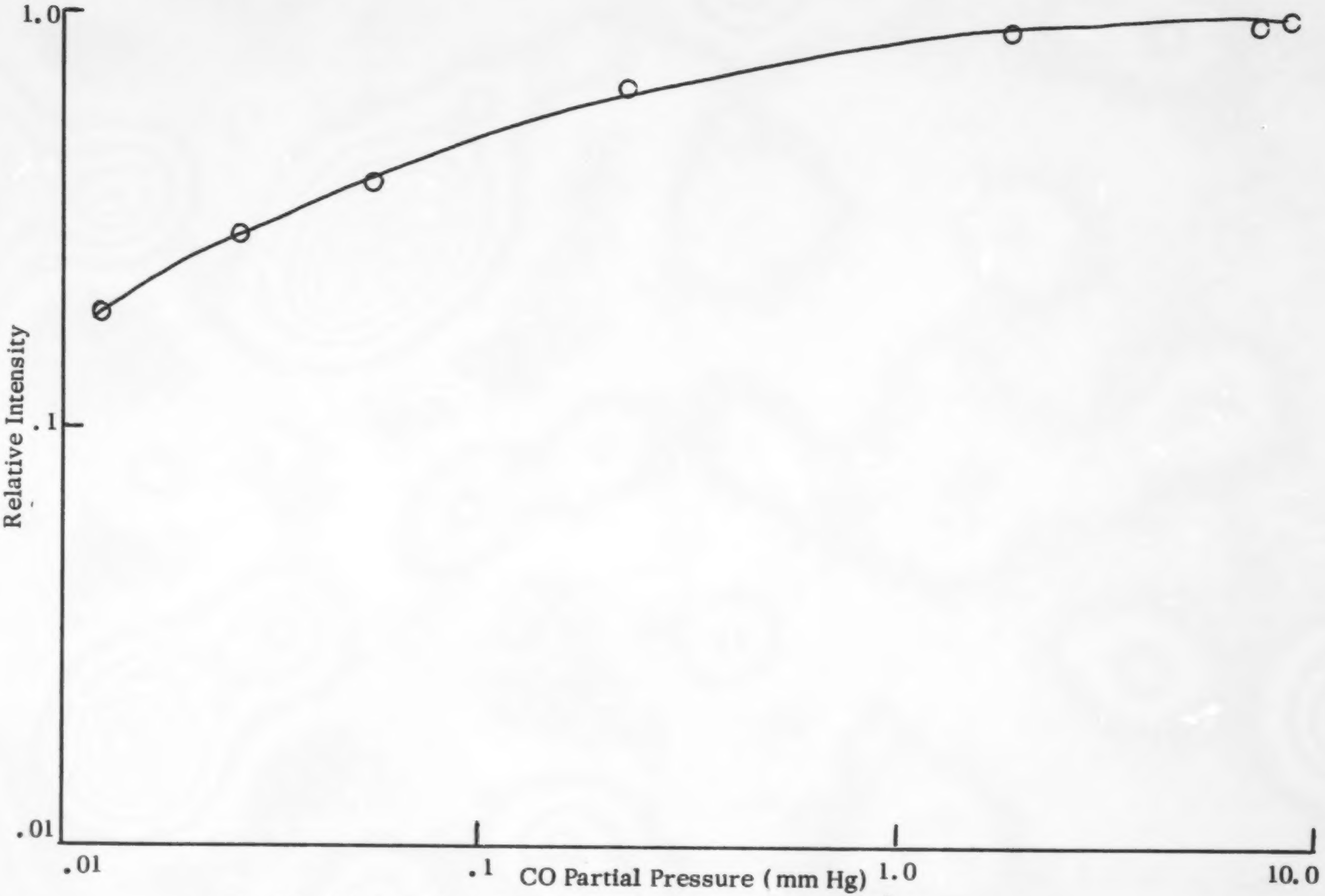

Fig. 50. Carbon Monoxide Calibration Curve 2160 cm^{-1}.

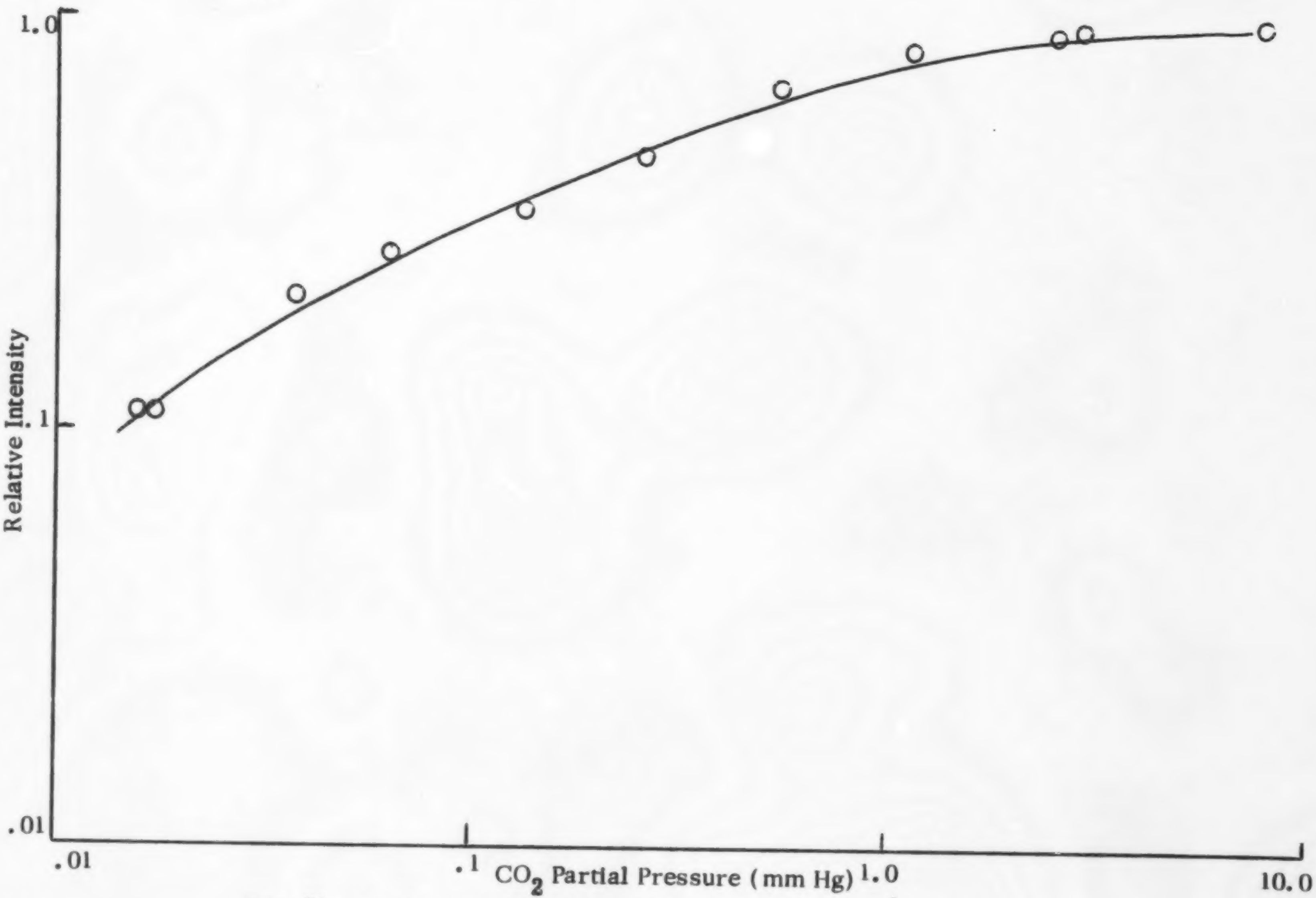

Fig. 51. Carbon Dioxide Calibration Curve 3640 cm^{-1}.

I. Nitrosylsulfuric Acid

A classical wet chemical analysis method is being used to analyze the liquid effluents from the scrubber and the stripper to determine the nitrogen oxide content of the streams. Aliquots of the acid solutions are titrated with potassium permanganate (0. 1M) which acts as its own indicator, to a faint pink end point which remains for at least 5 min. It may be noted that, near the end of the titration, the reactions involved proceed more slowly due to the very low concentration of $NHSO_5$ remaining. This procedure depends on the hydrolysis of the $HNSO_5$ to HNO_2 which is then oxidized by the permanganate to HNO_3:

$$NHSO_5 + H_2O \rightarrow H_2SO_4 + HNO_2$$

$$5\ HNO_2 + 2\ HMnO_4 \rightarrow HNO_3 + 3\ H_2O + 2\ Mn\,(NO_3)_2$$

One problem with this technique is that it will not accurately determine any excess dissolved NO_2, which is hydrolyzed to an equimolar mixture of HNO_2 and HNO_3. Since the nitric acid cannot be oxidized any further, the permanganate will not react with half of the NO_2 dissolved in the acid. (It should be emphasized that all the NO_2 associated with N_2O_3 will be determined because no HNO_3 is obtained when the N_2O_3 is hydrolyzed.) This will probably not be a significant problem since very little NO_2 should be dissolved in the acid.
The technique has been tried several times in the laboratory and has shown good reproducibility (about 1%).

One precaution that will be necessary is to avoid very high concentrations of sulfuric acid in the analysis. Titration of 50% nitrosylsulfuric acid in 98% H_2SO_4 with 0. 1 molar $KMnO_4$ resulted in the liberation of a great deal of heat which caused the nitrosylsulfuric acid to break down with the resulting evolution of brown NO_2 fumes which were lost to the analysis. When diluted with 80% sulfuric acid so that the H_2SO_4

and $HNSO_5$ concentrations were lower (about 2% $HNSO_5$), the temperature did not rise as much during the titration and no NO_2 evolution was evident. Care must be taken to add the permangate solution sufficiently slowly so as to avoid significant heating of the nitrosyl solutions. The use of a surrounding ice bath may be employed.

J. Sulfuric Acid

Sulfate will be analyzed using the standard barium sulfate gravimetric technique whereby the solution is treated with an excess of a barium chloride solution and the resulting $BaSO_4$ precipitate is washed and weighed. This procedure was tried several times in the laboratory and it appears that it is the type of procedure that takes experience to perfect. The precipitate has to be properly washed and dried before being weighed, but once this technique is mastered, good results can be obtained.

K. Total Acidity

Acid solutions will be titrated with standard sodium hydroxide to obtain the total H^+ content.

L. Water

The water content of gas streams will be measured through the use of a hygrometer. The primary application for this technique will be in the incoming flue gas line where the hot flue gas from the natural gas burner (with a 20% water content) is diluted to a cooler gas (about 400 °F) with a 5% water content. The hygrometer will be put in a cooled side stream (about 100 °F) which will then be vented. The water content of the incoming flue gas can be adjusted by changing the dilution ratio. The side stream will also allow variation in the flue gas flow without changing the burner or dilution settings.

APPENDIX 3. Visit to an Operating Chamber Plant

On August 9, 1969, Dr. Keilin and Mr. Walitt visited a Chamber Process Sulfuric Acid Plant operated by U. S. Steel Agri-chemicals, a subsidiary of U. S. Steel engaged in fertilizer manufacture. The plant was located in Nashville, Tennessee, and produced sulfuric acid exclusively for use in an adjacent fertilizer plant.

There was interest in visiting an operating plant for two reasons. First, the Tyco/EPA Modified Chamber Process for removal of sulfur dioxide from power plant flue gas is very similar to the original Chamber Process and we wanted to get a good idea of actual plant operating characteristics. Second, the newly modified Catalytic Chamber Process could well improve the process economics of the Chamber Process to a degree where it could again compete with the Contact Process, and it was therefore important to determine the real limitations of the old process. U. S. Steel Agri-chemicals (formerly Armour Agri-chemicals) was quite cooperative and invited us to see their acid-making facilities.

Discussions with engineering and managerial people at the Agri-chemical headquarters in Atlanta revealed two significant facts: (1) they are phasing out all Chamber Process plants because it has become cheaper to buy acid than to make it this way and (2) no one has bothered to study the Chamber Process closely enough to understand its basic chemistry and thus determine the fundamental problems that have caused the obsolescence of the process.

All new acid-making capacity being installed by Agri-chemicals utilizes the contact process, although the product of the chamber process is ideal for use in fertilizer manufacture. Contact acid (either purchased or manufactured by Agri-chemicals) must be diluted back to 60° Bé (78%) before being used. Obviously, the low strength (also 78%) of the chamber process acid is not the limiting feature.

A tour of the Nashville plant and a detailed discussion of the process with Mr. Clifford Roquet, the "acid maker" in charge of the operation of the plant, gave an insight into the problems that have

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contributed to the obsolescence of the Chamber Process. The plant that was visited was in its last days of operation, but we were assured that operating conditions were typical.

The appearance of the plant was a revelation in itself. Everything was very old and in a poor state of repair. It had been built in 1895 and rebuilt in 1922 after a disastrous fire. There was little evidence that any design modifications had been made during rebuilding, and few changes have been made since then. (As a matter of fact, some of the drawings of Chamber plant equipment in Lunge's book "Sulfuric Acid and Alkali," printed in 1891, looked very much like equipment in this plant.)

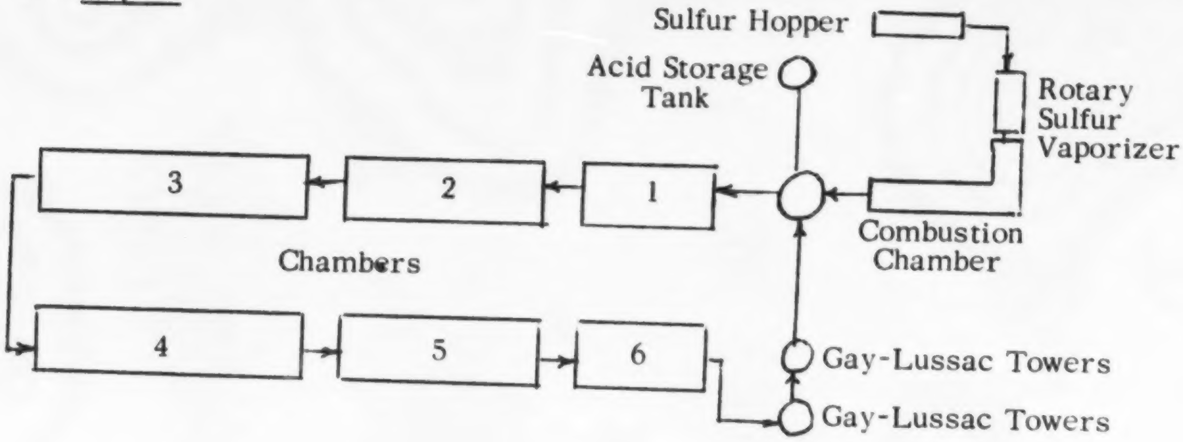
Figure 52 shows the layout of the Nashville plant and illustrates some of the known operating conditions. Because of the almost complete lack of instrumentation, no other significant data could be obtained concerning plant operation. Process control was crude and limited in scope. The primary control technique was to observe the color of the exhaust plume from the second Gay-Lussac tower and vary the SO_2-air balance in the combustion chamber accordingly. This ratio could be increased by putting bricks in the draft inlets in the furnace, thus cutting down the amount of influent air. The color of the plume varied from reddish brown (when too much NO entered the towers and was lost to the atmosphere where it was oxidized to NO_2), to white (when too much NO_2 entered the tower and was lost as nitric acid mist).

Despite the crudity of the operation, the plant consistently produced 776 tons per week of 60° Bé sulfuric acid for use in the adjacent fertilizer plant. There was little or no unscheduled down-time, and only two men per shift were needed to operate the entire plant. In addition, examination of production economics showed that the cost of the sulfur raw material contributed up to 70% of the total manufacturing cost of the acid. Why then are chamber plants obsolete?

The answer to this question involves an examination of the sulfuric acid industry as a whole and Agri-chemicals' plans for the future. Although the Nashville plant was operating relatively smoothly, it was obviously due

Fig. 52. Layout and Operating Conditions of U. S. Steel Agri-Chemical Chamber Process Sulfuric Acid Plant, Nashville, Tennessee

A. Layout


Sulfur Hopper
Acid Storage Tank
Rotary Sulfur Vaporizer
3
2
1
Combustion Chamber
Chambers
4
5
6
Gay-Lussac Towers
Gay-Lussac Towers

B. Operating Conditions

1. Production: 600 tons (100%) per week as 60° Bé (77.7%).
2. H_2SO_4 recycle flow: 3.5 times acid production.
3. NO_x recovery: 32 oz (as $NaNO_3$) per ft^3 of recycle acid in Gay-Lussac tower
4. NO_2/SO_2 mole ratio in first chamber: 0.05

C. Chamber Conditions

Chamber No.	Dimensions	Temperature, °F	Product Acid
1	50 x 28 x 20	286	None
2	75 x 28 x 20	272	None
3	110 x 28 x 20	252	52° Bé
4	110 x 28 x 20	230	52° Bé
5	75 x 28 x 20	212	52° Bé
6	50 x 28 x 20	166	52° Bé

for replacement before too long. Agri-chemicals was faced with the choice of either building or buying. They found that they could buy 66° Bé acid from a manufacturer who used a smelter off-gas as his raw material in a contact plant and could deliver it to the Nashville fertilizer plant (by barge) cheaper than the old chamber plant could make it. This points up the fact that when the sulfur raw material is available to the acid manufacturer at no cost, he can produce acid at a very attractive price compared to acid manufactured by conventional means. This would be true for acid made from power plant stack gas as well as smelter off-gas.

Obviously , if Agri-chemicals wanted to make the acid and compete with this supplier's price, they would have to change their manufacturing approach and find a way to cut costs. One way they have tried is to make larger quantities at a single location and ship the acid to the various fertilizer plants. This is where the basic problems with Chamber Plants become apparent.

There are essentially two reasons why you cannot build large Chamber Plants and ship the acid to where it is needed: (1) it costs too much to ship 78% chamber acid, and (2) equipment size makes it impractical to build a Chamber Plant of greater than 100-ton-per-day capacity. Both problems were examined in some detail to see if they were unavoidable for fundamental reasons.

Why can't high strength acid be made in a Chamber Plant? After much discussion with Agri-Chemical people, we concluded that our original reason must be correct: the extreme difficulty of recovering oxides of nitrogen from high acid strength nitrose. Normally, in the Glover tower, the 60° Bé acid from the Gay-Lussac tower is diluted with the 52° Bé acid from the chambers and contacted with hot combustion gas (1600 °F) from the sulfur burner which heats the dilute acid and vaporizes the dissolved N_2O_3. Since the solubility of N_2O_3 increases with acid concentration, excessively high temperatures would be required to raise the N_2O_3 vapor pressure to effect nitrogen oxide recovery from nitrose of higher acid strength. To achieve these elevated temperatures without creating the requirement for additional heat in the system, the L/G ratio would have to be reduced. This in turn means that the nitrose would have to be more concentrated in N_2O_3 to supply the required nitrogen oxide catalyst which would therefore require more heat for N_2O_3 removal, etc. It appears that trial-and-error optimization have resulted in a process that uses an acid recycle of 3.5 times the acid production rate and a product concentration of 60° Bé.

An understanding of the second problem, excessively large equipment, requires an examination of what is going on in the lead chambers. These large structures serve two purposes: (1) to provide an adequate volume for reoxidation of the NO formed when NO_2 oxidizes SO_2, and (2) to provide a large surface area for dissipation of the heat generated by the SO_2 oxidation and the absorption of SO_3 in the water spray. Re-examination of the plant operating conditions in Fig. 46 shows that the NO_2/SO_2 ratio is 0.05, which means that the chamber volume has to be big enough to allow the NO to be reoxidized 20 times before all the SO_2 is oxidized. At first glance, this would seem to be very inefficient considering the slow rate of NO oxidation, but if the NO_2/SO_2 ratio were increased substantially, the heat generated in the first chamber would be too much to be dissipated by this inefficient box-like structure. The solution to the problem was to keep the NO_2 dilute and add more boxes. The rule of thumb used in the industry is 5 ft^3 per lb of H_2SO_4 produced per day. Even the more efficient Mills-Packard towers require about 2.5 ft^3 per lb of H_2SO_4 produced per day. After considering these problems, it is clear that any attempt to build a 500 to 1000 ton per day chamber sulfuric acid plant in the conventional manner is doomed.

How then does all this affect the prospects for the development of the Tyco/EPA Catalytic Chamber Process for the removal of SO_2 from power plant flue gas? The problem of manufacturing a low strength acid does not exist, since the catalytic stripper enables us to recover the oxides of nitrogen from high acid strength nitrose (up to 92%) without having to worry about vapor pressure limitations. The catalytic process operates at low temperature and permits N_2O_3 recovery from cool gases, such as the 300 °F power plant stack gas.

The problem of equipment size is somewhat complex, but does not depend on the same limitation as the conventional Chamber Plant. In the Catalytic Chamber Process, the SO_2 from the flue gas is mixed with NO_2 in the ratio of $NO_2/SO_2 = 2/1$, thus eliminating the need for the NO to be reoxidized in the gas phase. In addition, the heat dissipation requirement is eliminated because the gases are very dilute (0.3% as compared to 10 to 12% in chamber plants), and the SO_3 formed is not dissolved in water in the reactor. These factors tend to reduce the required chamber volume problems to the point where they can probably be eliminated completely. With no excess heat to dissipate, no NO reoxidation, and no sulfuric acid absorption, it is likely that the last remaining function of the chambers, SO_2 oxidation, can be carried out in the connecting duct work.

Although multiple towers will be required for nitrogen oxide absorption and recovery, the catalytic nature of the Glover tower equivalent (stripper), which requires very little stripping gas to effect nitrogen oxide recovery, should help reduce the size of the equipment.

All things taken into account, we found no fundamental properties of Chamber Plants that would create potential problems for the Tyco/EPA Catalytic Chamber Process for SO_2/NO_x pollution control. In addition, it seems likely that the new process can be adapted to the more concentrated gases of a sulfur burner to permit the production of 66° Bé acid and perhaps high strength oleums.

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